STUDY OF DECREASED T SITE-SYMMETRY IN THE MIXED CRYSTALS $Ag_3(PO_4,AsO_4)$

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The system Ag_3PO_4–Ag_3AsO_4 has been studied by X-ray analysis of the powder samples and infrared absorption spectra. Formation of cubic mixed crystals of the substitution type has been found within the whole concentration range. For the tetrahedral anions at the site $T(2)$ lowering of the site-symmetry to the effective site-symmetry C_3 has been found on the basis of the site- and factor-group analyses of the space group T_d^4.

This report deals with study of formation of mixed crystals in the system $Ag_3(PO_4, AsO_4)$ with special respect to the problem of lowering of the site-symmetry of the tetrahedral anions. This lowering can be interpreted with the mixed crystals where the respective dilution excludes mutual action of vibrations of the same particles in the primitive (spectroscopical) elementary cell with the number of formula units above unity, *i.e.* the spectrum is interpreted of the particle "diluted" in an isostructural mixed crystal.

In the studied system the size of the anions and the other crystallochemical parameters allow formation of mixed crystals in the whole concentration range[1]. In the systems studied so far, $Ag_3(PO_4, VO_4)$ (ref.[2]) and $Ag_3(AsO_4, VO_4)$ (ref.[3]), different structure allowed such studies within an only limited concentration range.

EXPERIMENTAL

The mixed crystals $Ag_3((PO_4)_x(AsO_4)_y)$ where $x + y = 1$ were prepared by precipitation of aqueous solutions containing $(NH_4)_2HPO_4$ and Na_2HAsO_4 (total concentration $0.02M$) with a $0.1M$-$AgNO_3$ solution. The yields were within 85 to 90%, because the mixed crystals partially dissolved in the formed acid medium (HNO_3). The crystals were very fine and their colour varied from light yellow (Ag_3PO_4) to dark brown (Ag_3AsO_4). The crystalline precipitates formed were decanted with water until negative reaction of NH_4^+ and Ag^+ ions and dried at room temperature in dark. Ag and As were determined as AgCl and As_2S_5, respectively, the phosphorus content was obtained by calculation[4].

The X-ray analysis of the polycrystalline samples was carried out with a Geigerflex difracto-graph (Rigaku Denki, Japan), Co anode, Fe filter, Geiger–Müller detector. Indexing of the d values, determination of the lattice parameters and selection of the admissible space groups of the cubic system were carried out by our own program[5] with a Tesla 200 computer.

The infrared spectra were measured with a grating spectrophotometer Perkin–Elmer 325 in KBr disc (13 mm diameter) within the region 4000 to 200 cm^{-1} using the ordinates 1—4.

RESULTS AND DISCUSSION

The crystallographical data necessary for interpretation of IR spectra are taken from literature. The low-temperature modification[6] of Ag$_3$PO$_4$ is isostructural and isomorphous with Ag$_3$AsO$_4$ (ref.[7]). The both substances crystallize in the cubic space group T_d^4, $Z = 2$, the atoms Ag, P (or As) and O being at the sites $S_4(6)$, $T(2)$ and $C_3(8)$, respectively. The lattice parameter of Ag$_3$AsO$_4$ is greater by 2% than that of Ag$_3$PO (601 pm).

X-Ray Analysis

Table I gives the lattice parameters of pure compounds of the mixed crystals determined from experimental inter-plane distances (10 to 12 values). Dependence of the lattice parameters of the mixed crystals on their composition obeys the Vegard law[8] within experimental error. The lattice parameter of the cubic substitution mixed crystals increases from the value 600 ± 1 pm (for Ag$_3$PO$_4$) to 612 ± 1 pm (for Ag$_3$AsO$_4$). Indexing of every individual X-ray photograph excludes 27 out of total 36 cubic space groups, the remaining 9 primitive space groups involving the $T_d^4 -$ $- P\bar{4}3n$ group, i.e. the group found unambiguously[6,7] for single crystals of the starting silver phosphate and arsenate.

Infrared Spectra

Steger and Schmidt[9] studied the infrared spectrum of Ag$_3$PO$_4$ considering its structure, Steger and Danzer[10] studied the spectra of the mixed crystals Ba$_3$(PO$_4$,AsO$_4$)$_2$ and Sr$_3$(PO$_4$, AsO$_4$)$_2$ (structure of the pure phosphates is D_{3d}^5, $Z = 1$).

Normal vibrations of the tetrahedral anions are realized in four non-reducible representations A$_1$ + E + 2F$_2$ belonging to the vibrations ν_1 to ν_4. Due to the coincidence of the vibrations $\nu_2(\text{PO}_4) \sim \nu_4(\text{AsO}_4) \sim 400$ cm^{-1} and $\nu_1(\text{AsO}_4) \sim$ $\sim \nu_3(\text{AsO}_4) \sim 820$ cm^{-1} the vibrations given in Table I only can be used for study of correlations. The narrow band of the vibration $\nu_1(\text{AsO}_4)$ is not observable in the region 820 cm^{-1}, and its coincidence with the vibration band $\nu_3(\text{AsO}_4)$ does not prevent exploitation of the antisymmetrical valence vibration, because shape of the absorption band of this vibration is not affected.

In the primitive elementary cell T_d^4 ($Z_p = 2$) the site-symmetry of the anions is univocally $T(2)$, the cations being located at $S_4(6)$ according to X-ray analysis. From comparison of the correlation G$_M$ → G$_S$ → G$_F$, i.e. T_d → T → T_d (ref.[2]; the correlation T → T_d given in ref.[9] was not carried out in adequate way) with experimental spectra of the pure components and of mixed crystals (Table I) it follows that the

spectra correspond neither to the site-symmetry approach nor to the factor symmetry approach. According to these approaches for the pure compounds the activation of vibration $\nu_2(E)$ is forbidden (the both pure compounds show absorption at 400 cm^{-1} in their spectra) and for the mixed crystals activation of $\nu_1(A_1)$, $\nu_2(E)$ and activation of the second vibration in the region ν_3 and ν_4 are forbidden. Symmetry lowering of the anions $G_M \rightarrow G_V$ (symmetry lowering due to deformation of the tetrahedron to the own symmetry) is out of question, because all the P—O distances are equal (155 pm)[6].

The theory of vibrational spectra of molecular particles in a crystal lattice considering only the individual particles states that the internal degenerated vibrations of these particles (with the wave-numbers incomparable with those of the lattice vibrations) can be split by action of the external lattice vibrations[11]. Theoretically

TABLE I

Lattice Parameters and Infrared Spectra of Mixed Crystals $Ag_3(PO_4, AsO_4)$

Ag_3AsO_4 mol. %	a pm	PO_4^{3-}			AsO_4^{3-}	
		$\nu_1(A_1)$	$\nu_3(F_2)$	$\nu_4(F_2)$	$\nu_2(E)$	$\nu_3(F_2)$
0	600 ± 1	—	1 010 br	555	—	—
10·4	601 ± 1	—	1 010 br	550	350 w	830, 780
20·2	603 ± 1	980 sh	1 050, 1 010 sh	540	345 sh	830, 790 sh
30·1	604 ± 1	990 sh	1 035, 1 010 sh	550	350 sh	835, 790
42·5	606 ± 1	—	1 010	550	350 sh	820
51·2	606 ± 1	990 sh	1 035, 1 010	665, 550	350 sh	830, 790 sh
60·7	607 ± 1	980	1 040, 1 010	665 sh, 550	350 sh	830, 780
70·3	608 ± 1	970	1 040, 1 010	660 sh, 550	350 sh	825, 775
80·1	609 ± 1	980	1 040, 1 010	660 sh, 550	350 sh	825, 780
90·2	610 ± 1	970	1 040, 1 010	660 sh, 545	340 sh	825, 775
100	612 ± 1	—	—	—	330	825, 785 sh

TABLE II

Correlation Table of Sub-Groups of the Group T

Vibration	T	C_3	D_2	C_2
ν_1	A	A(IR)	A	A(IR)
ν_2	E	E(IR)	2 A	2 A(IR)
ν_3, ν_4	F(IR)	A(IR) + E(IR)	B_1(IR) + B_2(IR) + B_3(IR)	A(IR) + 2 B(IR)

this symmetry lowering can be predicted from the square of representation of the considered degenerated vibration. As the bases of the representations are identical, symmetrical products of the representations were derived $[\chi(E)]_2 = A + E$ and $[\chi(F)]_2 = A + E + F$. From these expressions of the degenerated representations E and F of the site-group T it can be seen that, in this approach, internal vibration type E is not split, it can only be activated. The internal vibration type F can be split by the lattice vibrations type F, because translation and rotation coordinates *i.e.* $T(F)$ and $R(F)$ belong to this representation in T group, and this representation is involved in the symmetrical square.

A single sub-group C_3 (Table II) in the correlation table of the sub-groups of the group T corresponds to the experimental splitting of the vibration type F into two components. However, for this correlation activation of the vibration type E is necessary, which was proved experimentally. At the same time the symmetrical valence vibration type A is activated in this group, which was proved in the case of the phosphate and mixed crystals containing less phosphate than 40 mol.%. The correlation of the site-group to the effective site-group, *i.e.* $T \rightarrow C_3$, is most conclusive in the case of the phosphate with the concentration about 10 to 39 mol.% Ag$_3$PO$_4$. It is just this region in which dilution prevents possible mutual influence of the phosphate anions in the primitive elementary cell ($Z_P = 2$). Similar situation is encountered with the arsenate anion at the concentrations about 10 to 30 mol.% Ag$_3$AsO$_4$. The mentioned regions represent the dilution of the given anion in the mixed crystal which excludes interlocking of the internal vibrations of the particles in the primitive elementary cell, which results in more clean-cut absorption bands enabling their better separation. Under these conditions and with exclusion of the factor symmetry it is possible to study the manifestations of the site-symmetry (so called first approach) which, in this and several other cases[2,3], decreases the effective site-symmetry, *i.e.* the correlation $T_d \rightarrow T \rightarrow C_3$ is observed.

REFERENCES

1. Čáp J.: *Thesis.* Prague Institute of Chemical Technology, Prague 1976.
2. Hájek B., Muck A., Smrčková O.: This Journal *44*, 823 (1979).
3. Hájek B., Muck A., Smrčková O.: This Journal *44*, 3346 (1979).
4. Tomíček O.: *Kvantitativní analysa*, 3rd. Ed. p. 46. Státní Zdravot. Nakl., Prague 1954.
5. Muck A., Ondráček J., Hájek B.: Sb. Vys. Šk. Chemicko-Technol. Praze B*24*, 19 (1979).
6. Masse R., Tordjman I., Durif A.: Z. Kristallogr. Kristallgeometrie *144*, 76 (1976).
7. Helmholz L., Levin R.: J. Amer. Chem. Soc. *64*, 354 (1942).
8. Vegard L.: Z. Phys. *12*, 289 (1923).
9. Steger E., Schmidt W.: Ber. Bunsenges. Phys. Chem. *68*, 102 (1964).
10. Steger E., Danzer K.: Ber. Bunsenges. Phys. Chem. *68*, 635 (1964).
11. Hornig D. F.: J. Chem. Phys. *16*, 1063 (1948).

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