A STUDY OF MIXED CRYSTALS IN THE $InPO_4$-$InVO_4$ SYSTEM AND THEIR INFRARED SPECTRA

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The crystal symmetry was studied for mixed crystals in the $InPO_4$–$InVO_4$ orthorhombic system. The infrared spectra were examined using the site group and factor group approach, and the $T_d \rightarrow C_s \rightarrow C_{2v}$ correlation was found more appropriate than the $T_d \rightarrow C_{2v} \rightarrow D_{2h}$ correlation.

$InPO_4$ crystallizes in a single orthorhombic modification[1,2] the space group of which is D_{2h}^{17} – $Cmcm$ (ref.[3]). Its lattice parameters are $a = 530{\cdot}8$ pm, $b = 785{\cdot}1$ pm, $c = 676{\cdot}6$ pm; $Z = 4$ (refs[1,3,4]). The factor groups correlation for the vibrational spectra of $InPO_4$ agrees better with the space group C_{2v}^{12} which was also initially considered[3].

$InVO_4$ occurs in three crystal modifications. The structure of modifications I (541–682°C) and II (682–716°C) has not been determined, modification III (above 716°C) has a D_{2h}^{17} structure. All the modification transformations are irreversible[5]. The lattice parameters of $InVO_4$ III are $a = 576{\cdot}5(4)$ pm, $b = 854{\cdot}5(5)$ pm, $c = 659{\cdot}2(4)$ pm (refs[5–7]). $InVO_4$ is amorphous at temperatures lower than 541°C and it melts incongruently at 1 134°C. No infrared spectra could be found in the literature for $InVO_4$.

The present work is devoted to the formation of mixed crystals in the $InPO_4$–$InVO_4$ system and their infrared spectra.

EXPERIMENTAL

Samples of the pure components and their mixed systems were prepared by solid state reaction using In_2O_3, V_2O_5 and $(NH_4)_2HPO_4$ as the starting compounds in the appropriate molar ratios. The ground mixtures were annealed at 1 000°C for 2 h, allowed to cool down, ground to powder, annealed at the same temperature, ground again, and annealed at 1 000—1 080°C for 3 h. A series of powder samples was prepared in 10 mol.% increments; 5 mol.% samples were also prepared in the two side regions. The colour of the samples varied from brown ($InVO_4$) through ochre to white ($InPO_4$).

The X-ray diffraction patterns were obtained with a Geigerflex instrument (Rigaku Denki) equipped with a Cu anode and a Ni filter, at $\Theta = 0-25°$ ($0-30°$ for the side concentrations).

The infrared spectra of the powder samples over the region of 4 000—200 cm^{-1} were measured at room temperature on a Perkin-Elmer 325 spectrophotometer in KBr disks.

RESULTS AND DISCUSSION

Statistical Evaluation of the X-Ray Diffraction Measurements

The lattice parameters of the pure substances and their mixed crystals were refined by the least squares method using the X RAY-72 program of the University Com-

TABLE I

Structure data for pure $InPO_4$ and $InVO_4$. Dimensions and distances in pm

Data	$InPO_4$ (ref.[1])	$InVO_4$
a	530·8(5)	576·5(4)
b	796·9(6)	854·2(5)
c	676·4(5)	659·2(4)
$(X—O)_{XO_4}$	2 . 153·8	2 . 166·2(3) (ref.[6])
	2 . 156·1	2 . 179·1(3)
$(O—O)_{XO_4}$	4 . 252·2	271·7(4) (ref.[6])
	254·4	4 . 280·4(4)
	254·8	299·0(4)
In—O	4 . 219·2	4 . 216·2(3) (ref.[6])
	2 . 200·5	2 . 216·0(3)
Coordination number of In^{3+}	6	6
Symmetry of the InO_6 coordination polyhedron	distorted octahedron C_{2v}	distorted octahedron D_{2h}
Own symmetry of the XO_4 anion	C_{2v}	C_{2v}

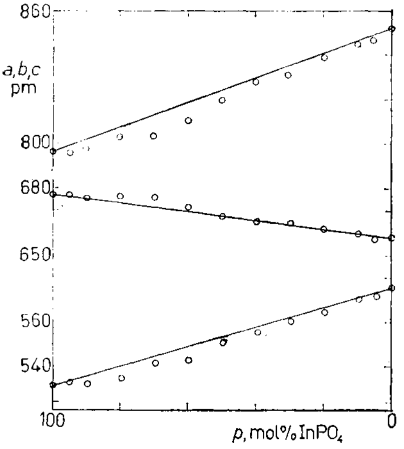

FIG. 1

Dependence of the lattice parameters on the concentration of the components in the $InPO_4$–$InVO_4$ system (parameters increase in order *a*, *c*, *b*). The straight lines show the ideal course obeying Vegard's rule puter Centre in Prague; $(hkl)_{InVO_4}$ indices were attributed to samples with more than 50 mol.% $InVO_4$ and $(hkl)_{InPO_4}$ indices to samples with 60 mol.% and more $InPO_4$ ($V_{InPO_4} = 287{\cdot}58 \,.\, 10^6$ pm^3, $V_{InVO_4} = 322{\cdot}88 \,.\, 10^6$ pm^3). The lattice parameters for the pure substances agree with published data (Table I).

The dependence of the refined lattice parameters on the system composition was evaluated with respect to Vegard's rule[8] using the linear regression approach. The correlation coefficients obtained for the dependences of the lattice parameters a, b, and c on the system composition, in mol.% (Fig. 1), are $r = -0{\cdot}9935$, $-0{\cdot}9903$, and $0{\cdot}9838$, respectively, indicating that the linear relation fits the actual dependence well. The regression lines are not presented in Fig. 1; the straight lines drawn only show the ideal shape of the dependences from one pure component to the other according to Vegard's rule. It can be concluded that the lattice parameters of In(PO_4, VO_4) mixed crystals obey Vegard's rule.

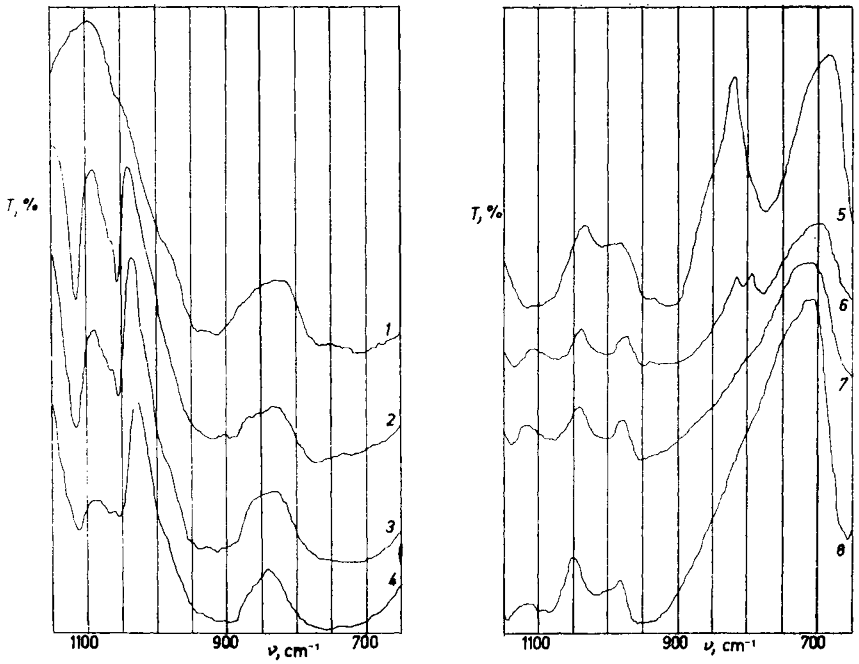

FIG. 2

Infrared absorption spectra for the $InPO_4$–$InVO_4$ systems in the ν_1 and ν_3 stretching vibration regions. $InPO_4$ content (mol.%): *1* 0 (pure $InVO_4$), *2* 5, *3* 10, *4* 20, *5* 80, *6* 90, *7* 95, *8* 100 (pure $InPO_4$)

Infrared Spectra

The infrared spectra of pure $InPO_4$ prepared from solid In_2O_3 and $(NH_4)_2HPO_4$ agree with those of the substance prepared by precipitation[1]; they are, however, less clear-cut and the splitting of the degenerate vibrations is incomplete. Two expressive absorptions appear in the $\nu_2(E, T_d)$ region, *viz.* at 305 and 268 cm^{-1}.

In the spectrum of pure $InVO_4$, the $\nu_3(F_2, T_d)$ vibration is split into two broad bands at 960–900 and 800–680 cm^{-1}. The first band involves also the $\nu_1(A_1, T_d)$ vibration which is activated in the C_{2v} or C_s site symmetry. The $\nu_2(E, T_d)$ vibration is again split into two bands over the 290–265 cm^{-1} range, as can be seen in the correlation table for C_{2v}^{12} structure (Table III in ref.[1]) for the $G_M \rightarrow G_S$ symmetry lowering of the ν_2 vibration. The spectra of both $InPO_4$ and $InVO_4$ can be better interpreted in terms of the $T_d \rightarrow C_s \rightarrow C_{2v}$ correlation than the $T_d \rightarrow C_{2v} \rightarrow D_{2h}$ correlation.

The spectra of the mixed crystals with 5 and 10 mol.% $InPO_4$ exhibit two distinct absorptions in the ν_2 vibration region, *viz.* at 300 and 265 cm^{-1}, which unambiguously point to the C_s site symmetry since for this site symmetry, $E(\nu_2, T_d) \rightarrow (A' + A'')$, whereas for C_{2v}, $E(\nu_2, T_d) \rightarrow (A_1 + A_2)$, where only A_1 is infrared-active. The situation is similar for low concentrations $InVO_4$. In mixed crystals with 10 mol.% $InVO_4$,

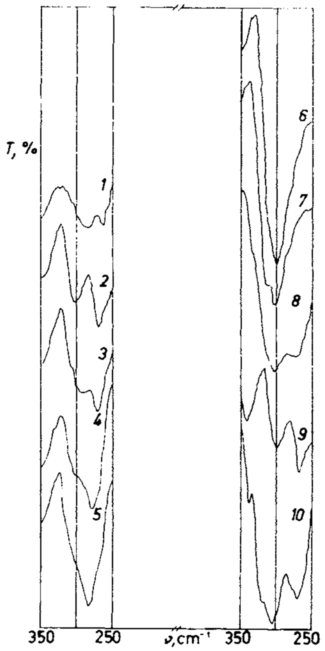

Fig. 3

Infrared absorption spectra for the $InPO_4$–$InVO_4$ systems in the ν_2 vibration region. $InPO_4$ content (mol.%): *1* 0 (pure $InVO_4$), *2* 5, *3* 10, *4* 20, *5* 30, *6* 70, *7* 80, *8* 90, *9* 95, *10* 100 (pure $InPO_4$)

the E type vibration is split from the initial $F_2(\nu_3, T_d)$ to $(A' + A'')$ (ν_3' and ν_3'' in C_s); the absorptions lie at 805 and 775 cm^{-1}. The A' type vibration from the initial $F_2(\nu_3, T_d)$ with activated $A'(\nu_3''', C_s)$ is included in the combined nonresolved band at 960–890 cm^{-1}. At 5 and 10 mol.% $InPO_4$, the $F_2(\nu_3, T_d) \rightarrow (2A' + A'')$ (C_s) or $(A_1 + B_1 + B_2)$ (C_{2v}) correlations, *i.e.*, the number of absorptions (1 115, 1 065 sh, 1 055 cm^{-1}) suit both for D_{2h}^{17} and for C_{2v}^{12}. The values for all the above absorption bands are seen in Figs 2–3.

The spectra of $InPO_4$ and $InVO_4$ in low concentrations in the mixed crystals are again better interpreted in terms of the $T_d \rightarrow C_s \rightarrow C_{2v}$ correlation, *i.e.* the C_{2v}^{12} space group.

REFERENCES

1. Hájek B., Šantavá E., Muck A.: This Journal *49*, 2252 (1984).
2. Deichman E. N., Tananaev I. V., Ezhova Zh. A., Kuzmina T. N.: Zh. Neorg. Khim. *13*, 47 (1968).
3. Mooney R. C. L.: Acta Crystallogr. *9*, 113 (1956).
4. Mooney R. C. L., Kissinger H., Perloff A.: Acta Crystallogr. *7*, 642 (1954).
5. Touboul M., Ingrain D.: J. Less-Common Metals *71*, 55 (1982).
6. Touboul M., Toledano P.: Acta Crystallogr., B *36*, 240 (1980).
7. Blasse G.: Philips Res. Repts. *23*, 344 (1968).
8. Vegard L.: Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem. *67*, 149 (1928).

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