

INFRARED SPECTROSCOPIC STUDY OF THE $\text{YPO}_4\text{-YCrO}_4$ SYSTEM

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The infrared spectra and powder X-ray diffraction patterns of polycrystalline $\text{YPO}_4\text{-YCrO}_4$ samples are studied from the point of view of their crystal symmetry. Mixed crystals of the D_{4h}^{19} symmetry are formed over the region of 0–30 mol.% YPO_4 in YCrO_4 . The $T_d \rightarrow D_{2d} \rightarrow D_2$ or $C_{2v}(G_{\text{S eff}})$ correlation is appropriate for both PO_4^{3-} and CrO_4^{2-} anions.

The structure of synthetic YPO_4 was determined by Strada and Schwendimann¹ as long ago as 1943; later, this investigation was extended and refined by Mooney and coworkers² and by Milligan and coworkers³. Mixed crystals containing YPO_4 were studied by Muck and coworkers^{4,5}.

The preparation and X-ray diffraction examination of YCrO_4 were the concern of Schwarz⁶ and of Buisson, Bertaut and Mareschall⁷. Y_2O_3 and CrO_3 were used by Schwarz as the starting substances and transformed into Y(OH)CrO_4 in aqueous solution, and this compound was heated in air at a rate of 150°C h^{-1} and annealed at 530°C to obtain YCrO_4 . Buisson and coworkers prepared this substance by annealing $\text{Y(NO}_3)_3$ with $\text{Cr(NO}_3)_3$ at 650°C under nitrogen. YCrO_4 decomposes to YCrO_3 and CrO_3 at 690°C .

Roy and Nag⁸ dealt with the preparation of lanthanoid chromates(V) and chromites by thermal decomposition of the tris(oxalatochromites); for YCrO_4 , however, this approach has not been tested, and for LaCrO_4 , ill-reproducible results were obtained by this method⁹.

The aim of the present work was to examine the possibility of formation of mixed crystals for the isostructural YPO_4 and YCrO_4 , which both belong to the tetragonal $D_{4h}^{19}\text{-I}4_1/\text{amd}$ space group ($Z = 4$) and whose lattice parameters match each other closely enough to make the mixed crystal formation feasible. The concentration region of this mixed crystal formation will be limited by the different symmetry of the structural groupings and by their different size. The temperature stability of YCrO_4 will also play a part, since its decomposition temperature is lower than the crystallization temperature of pure YPO_4 . It can be thus expected that the formation of mixed crystals, *i.e.* incorporation of PO_4 in the YCrO_4 lattice, will take place within a region of low YPO_4 concentrations.

EXPERIMENTAL

Attempts were made to prepare YCrO_4 by reacting Y_2O_3 with CrO_3 in the solid phase, in powder or in pressed pellets, at 600°C in air or in a stream of oxygen, but a mixture of Y_2O_3 , Cr_2O_3 and YCrO_3 invariably emerged. Good results, on the other hand, were obtained on reacting CrO_3 in aqueous solution with the stoichiometric amount of Y_2O_3 , evaporating to dryness, and heating the residue under oxygen at 250°C for 1 h and at 550°C for additional 6 h (YCrO_4 decomposes at temperatures higher than 600°C). The X-ray diffraction patterns of the dark green powder obtained were consistent with published data for YCrO_4 (refs^{6,7}).

For obtaining pure YPO_4 , a stoichiometric mixture of Y_2O_3 and $(\text{NH}_4)_2\text{HPO}_4$ was annealed under the same conditions as YCrO_4 . Since the substance so prepared contained some amount of $\text{P}_2\text{O}_7^{4-}$ giving rise to absorption at $1\,250\text{ cm}^{-1}$ in the infrared spectrum, 0.5 wt.% V_2O_5 was added in an attempt to prevent the formation of this impurity, with regard to the fact that YPO_4 free of $\text{P}_2\text{O}_7^{4-}$ can be obtained by reacting Y_2O_3 with $(\text{NH}_4)\text{HPO}_4$ at a temperature of 900°C if 1 wt.% V_2O_5 has been added¹⁰, whereas otherwise a temperature as high as $1\,100^\circ\text{C}$ has to be used⁴. In our case, however, the addition of V_2O_5 had no positive effect.

For the preparation of the YPO_4 - YCrO_4 mixed crystals, the starting components, *viz.* Y_2O_3 , CrO_3 , and $(\text{NH}_4)_2\text{HPO}_4$, in proportions covering the entire concentration region were homogenized by dispersing in water, evaporated to dryness, ground to powder, and annealed under conditions as above.

The powder X-ray diffractograms over the region of $\theta\ 2$ – 30° were obtained on a Geigerflex instrument (Rigaku Denki) with a Cu anode and an Ni filter; gain 2 000, rate 2. The infrared spectra were measured on a Perkin-Elmer 325 spectrophotometer over the region of $4\,000$ – 200 cm^{-1} in KBr disks.

RESULTS AND DISCUSSION

X-Ray Diffraction Patterns

The crystallographic data for YPO_4 were taken from the literature¹⁻⁵, those for YCrO_4 published in refs^{6,7} were verified by our X-ray diffractograms (Table I).

The lines of pure YCrO_4 were indexed by using the graphical method¹¹, the lattice parameters of pure YCrO_4 as well as of the mixed crystals (Table II) were refined by the least squares method using the X RAY-72 program of the University Computer Centre in Prague.

Over the region of 0–30 mol.% YPO_4 , the diffraction lines correspond to pure YCrO_4 and do not exhibit any shift to higher θ values. This gives evidence that mixed crystals with the D_{4b}^{19} structure are formed within this region. No more than two of the most intense lines of Y_2O_3 are observed (Table III), which indicates that unreacted Y_2O_3 is present in a low amount only. By contrast, all the more intense lines can be attributed to Y_2O_3 for samples with higher theoretical YPO_4 contents (40 mol.% and more) and mixed crystals do not form within this region.

Infrared Spectra

The infrared spectra indicate that samples with 5, 10, 20, and 30 mol.% YPO_4 contain CrO_4^{3-} and are free from $\text{P}_2\text{O}_7^{4-}$. Mixed crystals occur in this concentration range. On the other hand, no CrO_4^{3-} is present in the samples with 40 and more mol.% YPO_4 ; $\text{P}_2\text{O}_7^{4-}$ is absent from the sample with 40 mol.% YPO_4 but it is present in all samples containing 50 and more mol.% YPO_4 (Table IV, Fig. 1).

TABLE I
Structure data of YPO_4 and YCrO_4 (D_{4h}^{19})

Parameter	YPO_4^a	YCrO_4
a , pm	688.17(5)	712.1(2)
c , pm	601.77(6)	626.3(2)
(X—O) $_{\text{XO}_4}$ distance, pm	$4 \times 154.3(3)$	4×166.9
(O—O) $_{\text{XO}_4}$ distance, pm	$2 \times 240.9(6)$ $4 \times 257.4(5)$	4×279.0 2×259.2
Y—O distance, pm	$4 \times 230.0(4)$ $4 \times 237.3(3)$	2×232.1 4×245.0
Coordination number of Y^{3+}	8	6
Symmetry of the coordination polyhedron	dodecahedron (bisbisphenoid)	distorted octahedron
Own symmetry of the XO_4 anion	D_{2d} D_{2d}	C_{2v} D_{2d}

^a Ref.³.

TABLE II
Lattice parameters (pm) of $\text{YPO}_4\text{-YCrO}_4$ mixed crystals (D_{4h}^{19})

YPO_4 content mol.%	a	c
0	712.1(2)	626.3(2)
5	711.6(4)	625.0(5)
10	711.9(2)	625.6(3)
20	711.5(5)	625.2(7)
30	711.0(6)	625.8(14)

For the D_{4h}^{19} space group, the primitive elementary cell of YPO_4 or $YCrO_4$, with P or Cr in 4b position (D_{2d}), Y in 4a position (D_{2d}), and O in 16 h position (C_s), contains two formula units ($Z_p = 2$). At $k = 0$ the phonon dispersion curve includes 33

TABLE III
Number and intensity of diffraction lines of Y_2O_3 in YPO_4 - $YCrO_4$ mixed crystals

YPO ₄ content mol.%	Number of Y ₂ O ₃ lines	$d_{Y_2O_3}$ pm	I_{rel} %
0	0	—	—
5	1	306	4
10	0	—	—
20	1	306	14
30	2	433	11
		306	65

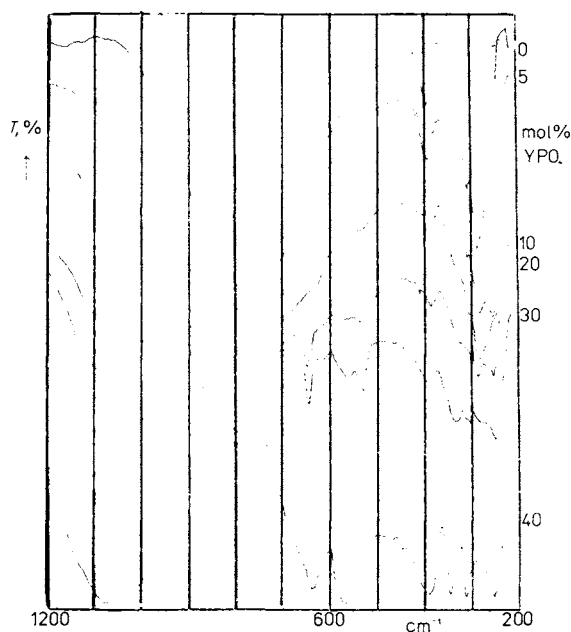


FIG. 1
Infrared spectra of YPO_4 - $YCrO_4$ mixed crystals (550°C)

optical branches ($3N - 3 = 36 - 3 = 33$), of them

$$\Gamma_{\text{internal}} = 2A_{1g}(\text{RA}) + 2B_{1g}(\text{RA}) + B_{2g}(\text{RA}) + 2E_g(\text{IR, RA}) + A_{1u}(\text{ia}) + 2A_{2u}(\text{IR}) + 2B_{2u}(\text{ia}) + 2E_u(\text{IR})$$

$$\Gamma_{\text{lattice}} = A_{2g}(\text{IR}) + 2B_{1g}(\text{RA}) + 3E_g(\text{IR, RA}) + A_{2u}(\text{IR}) + B_{1u}(\text{ia}) + 2E_u(\text{IR}).$$

For the interpretation of the spectrum of pure YCrO_4 , the basic correlation $T_d \rightarrow D_{2d} \rightarrow D_{4h}$ holds (Table V). Since, however, the effective site symmetry of CrO_4^{3-} is C_{2v} the correlation $T_d \rightarrow D_{2d} \rightarrow C_{2v}$ applies (Table V).

The totally symmetric $\nu_1(A_1, C_{2v})$ stretching vibration appearing as a shoulder at 880 cm^{-1} (not listed in Table IV) is infrared active, and so is the $\nu_2(A_1 + A_2(\text{ia}), C_{2v})$ symmetric bending vibration in the 300 cm^{-1} range which, however, does not manifest itself as in most tetraoxo metal complexes¹². The $\nu_3(A_1 + B_1 + B_2, C_{2v})$ antisymmetric stretching vibration gives rise to a broad band at 790 cm^{-1} . Two absorptions, at 420 and 395 cm^{-1} , appear in the region of the $\nu_4(A_1 + B_1 + B_2, C_{2v})$ antisymmetric bending vibrations of pure YCrO_4 . As the content of this component in the mixed crystals decreases, the corresponding band becomes better developed and the splitting more clear-cut (Table IV, Fig. 1), which indicates a complete removal of degeneracy. It can be inferred that the CrO_4^{3-} anion exhibits its C_{2v} effective site symmetry. This is consistent with the crystal symmetry theory, this C_{2v} symmetry of the anion being here lower than its D_{2d} site symmetry, and $C_{2v} \subset D_{2d}$.

The $\nu_3(\text{PO}_4)$ and $\nu_1(\text{PO}_4)$ regions are of no utility for the interpretation of the spectrum of phosphate in the mixed crystals, because no expressive splitting of $\nu_3(\text{PO}_4)$ and separation of ν_3 and ν_1 occur. The band of the $\nu_4(\text{PO}_4)$ vibration in the spectra of the mixed crystals with 20 and 30 mol.% YPO_4 is clearly split into three components, and since the dynamic effect of the crystal field (manifestation of the D_{4h} factor symmetry) can be ruled out at these concentrations, a lowering of the D_{2d} site symmetry to an effective site symmetry of at least D_2 or C_{2v} can be assumed. This is consistent with the theory¹³ because the symmetrized square of representation of the degenerate vibration, $[\chi(E)]_2 = A_1 + B_1 + B_2$, contains the B_2 representation belonging to the translational component of the $T(B_2)$ lattice vibration, which then brings about splitting of the degenerate E vibration and thus a $G_S \rightarrow G_{S\text{eff}}$ symmetry lowering. An additional lowering to C_2 or C_s or C_1 is conceivable, but this cannot be deduced from the spectrum because of the overlap of $\nu_2(\text{PO}_4)$ with the lattice vibrations or $\nu_2(\text{CrO}_4^{3-})$.

Since YCrO_4 decomposes at temperatures lower than the temperature of crystallization of YPO_4 (above 800°C), mixed crystals with low YCrO_4 content in YPO_4 could not be prepared, and so the site symmetry of CrO_4^{3-} in these mixed crystals could not be examined.

TABLE IV
Band positions (cm^{-1}) and relative intensities in the infrared spectra of $\text{YPO}_4\text{-YCrO}_4$ mixed crystals

YPO_4 content mol. %	$\nu_3(\text{PO}_4^{3-})$ and $\nu_1(\text{PO}_4^{3-})$	$\nu_3(\text{CrO}_4^{3-})$	$\nu_4(\text{PO}_4^{3-})$	$\nu_4(\text{CrO}_4^{3-})$	$\nu_2(\text{PO}_4^{3-})$ and lattice vibrations
0		790 b		420 vw, 395	325 sh, 305, 280
5	1 120 vw, 1 070 vw, 1 000 w, b	790 b	530 sh	420 vw, 390, 375 sh	325 vw, 305 vw, 280, 255
10	1 080 w, 1 050 w, 1 000 w	790 b	640 sh, 560 sh, 530 sh	420 sh, 390, 375 sh	335 sh, 305 sh, 280, 255 sh
20	1 120 vw, 1 065 sh, 1 030-1 015 b	800 b	645, 560 w, 530	420 vw, 385, 375	330 w, 303, 280, 250
30	1 115 w, 1 030-1 010 b	800 b	645, 555, 530	385, 375	340, 305, 280, 250

TABLE V
Correlation table for the crystal symmetry of XO_4^{3-} anions (X = P, Cr) in D_{4h}^{1g}

Value	T_d	D_{2d}	C_{2v}	$D_{2d} \rightarrow D_{4h}(\sigma_d \rightarrow \sigma_v)$
ν_1	$A_1(\text{RA})$	$A_1(\text{RA})$	$A_1(\text{IR}, \text{RA})$	$A_{1g}(\text{RA}) + B_{2u}(\text{ia})$
ν_2	$E(\text{RA})$	$A_1(\text{RA}) + B_1(\text{RA})$	$A_1(\text{IR}, \text{RA}) + A_2(\text{RA})$	$A_{1g}(\text{RA}) + B_{2u}(\text{ia}) + A_{1u}(\text{ia}) + B_{2g}(\text{RA})$
ν_3, ν_4	$F_2(\text{IR}, \text{RA})$	$B_2(\text{IR}, \text{RA}) + E(\text{IR}, \text{RA})$	$A_1(\text{IR}, \text{RA}) + B_1(\text{IR}, \text{RA}) + B_2(\text{IR}, \text{RA})$	$B_{1g}(\text{RA}) + A_{2u}(\text{IR}) + E_g(\text{IR}, \text{RA}) + E_u(\text{IR})$

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