

## Characterization of a Low-Temperature Form of $\text{InVO}_4$ \*

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A low-temperature form of  $\text{InVO}_4$ , belonging to the  $\alpha\text{-MnMoO}_4$  structural type, was characterized. The unit cell parameters were determined from X-ray powder diagrams. The infrared spectrum was discussed with the aid of a "site-symmetry analysis." The results were discussed in comparison with those of the corresponding high-temperature form ( $\text{CrVO}_4$  type) and with some other related compounds. © 1986 Academic Press, Inc.

### Introduction

As is known, heating of an equimolecular  $\text{V}_2\text{O}_5/\text{In}_2\text{O}_3$  mixture at temperatures around  $800^\circ\text{C}$ , leads to the formation of orthorhombic  $\text{InVO}_4$  (1, 2), which belongs to the  $\text{CrVO}_4$  structural type (3). Its vibrational spectrum, together with that of the structurally related  $\text{TlVO}_4$ , has been discussed in a recent paper (4).

On the other hand, it is possible to obtain a hydrated, amorphous  $\text{InVO}_4$  form, by precipitation from aqueous solutions. Heating of this material up to  $800^\circ\text{C}$  also produces the  $\text{CrVO}_4$ -like phase, but it has been claimed that one (5) or two (1) intermediate polymorphic phases exist.

By careful heating of amorphous  $\text{InVO}_4$  samples up to  $550^\circ\text{C}$ , we have obtained the modification called  $\text{InVO}_4(\text{I})$  by Touboul and Ingrain (1). Its X-ray powder diagram was similar but not identical to that pub-

lished by these authors. Interestingly, the infrared spectrum of this form closely resembled that of  $\alpha\text{-MnMoO}_4$  (6). Therefore, a structural relationship between the two compounds appears possible, and further studies carried out with this low-temperature form of  $\text{InVO}_4$ , clearly confirmed this supposition.

### Experimental

Samples of  $\text{InVO}_4(\text{I})$  were prepared according to the method described by Touboul and Ingrain (1): to an aqueous solution of  $\text{InCl}_3$  an equimolecular quantity of  $\text{NH}_4\text{VO}_3$  solution is added, under constant stirring and heating. The pH of the resultant mixture is adjusted to a value of 1, by addition of concentrated  $\text{HNO}_3$ . If a red precipitate is formed, the stirring and heating is continued after total redissolution. Then, a 3 N  $\text{NH}_4\text{OH}$  solution is added dropwise, and a bright yellow, gelatinous, and voluminous precipitate is quickly produced. The precipitate was filtered, washed with hot water, and dried over  $\text{P}_4\text{O}_{10}$  in a vacuum

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desiccator. The dried powder was then heated in a crucible furnace, in air, at 550°C during 3 hr.

Powder diagrams were obtained with a Philips PW-1010 diffractometer, using Ni-filtered  $\text{CuK}\alpha$  radiation. NaCl was employed as an external calibration standard. The indexing of the diagrams and the refinement of the cell parameters were made using a modified form of the program PIRUM of Werner (7) and employing an IBM-4330 computer.

The densities were determined pycnometrically at 25°C, using  $\text{CCl}_4$  as the working liquid.

The infrared spectra were recorded on a Perkin-Elmer 580 B spectrophotometer. The KBr-pellet technique was employed to obtain the spectra; the results were confirmed also using the Nujol-mull technique.

## Results and Discussion

### Crystal Data

The powder diagram of the investigated material closely resembles that of  $\alpha$ -MnMoO<sub>4</sub>; the structural relation predicted by the similarity of the IR spectra is thereby definitely supported.

The powder diagram also show, in all the prepared samples, the presence of small quantities of  $\text{In}_2\text{O}_3$  as an impurity. This impurification could be substantially dimin-

TABLE I  
CRYSTAL DATA FOR THE LOW-TEMPERATURE  
FORM OF  $\text{InVO}_4$

Crystal system: monoclinic Space group: $C2/m$
Structural type: $\alpha$ -MnMoO <sub>4</sub>
Lattice constants (Å) $a = 10.49(2)$
$b = 9.39(1)$
$c = 7.12(1)$
$\beta = 105.1(2)^\circ$
Unit cell volume = $677.4 \text{ \AA}^3$ $Z = 8$
Density: experimental = $4.6 \text{ g} \cdot \text{cm}^{-3}$
calculated = $4.50 \text{ g} \cdot \text{cm}^{-3}$

TABLE II  
X-RAY POWDER DIAGRAM OF THE  
LOW-TEMPERATURE FORM OF  $\text{InVO}_4$

$hkl$	$d_{\text{obs}}$	$d_{\text{calcd}}$	$I/I_0$
110/001	6.86	6.88	20
$\bar{1}11$	5.35	5.36	13
$\bar{2}01$	4.30	4.27	15
021	3.86	3.87	2
220	3.432	3.438	100
$\bar{3}11$	3.197	3.198	18
310	3.168	3.166	5
022	2.765	2.758	5
311	2.647	2.646	19
$\bar{1}32$	2.180	2.179	24
$\bar{1}51$	1.805	1.805	24
204	1.775	1.775	15
$\bar{1}52$	1.597	1.597	5
$\bar{4}24$	1.544	1.544	15

ished by using less than the stoichiometric amount of  $\text{InCl}_3$  in the precipitation of the amorphous precursors, but the presence of  $\text{In}_2\text{O}_3$  could never be totally avoided.

The crystallographic data for the low-temperature form of  $\text{InVO}_4$  are shown in Table I and the powder diagram, indexed with the given unit cell parameters, is shown in Table II. All the observed reflections satisfy the extinction rules of the space group  $C_{2h}^3 - C2/m$  (Nr. 12).

A comparison of the lattice parameters determined for  $\text{InVO}_4(\text{I})$  with those found for other structurally related phases, such as  $\beta$ -CdCrO<sub>4</sub> (8),  $\beta$ -FeMoO<sub>4</sub>,  $\beta$ -CoMoO<sub>4</sub>,  $\beta$ -MgMoO<sub>4</sub> (9), and  $\alpha$ -MnMoO<sub>4</sub> itself (10), shows that all of them exhibit very similar values. On the other hand, the comparison of the unit cell volume of  $\text{InVO}_4(\text{I})$  (with  $Z = 8$ ) and that of the corresponding high-temperature form (with  $Z = 4$ ) shows that the value corresponding to this later modification is slightly less than half of the former. This is also in accordance with the behavior found in other pairs of dimorphic phases of this type, in which the  $\text{CrVO}_4$  modification always presents a slightly

higher density than the  $\alpha\text{-MnMoO}_4$  form (cf. (8, 11)).

Finally, it was not possible to characterize the modification called  $\text{InVO}_4(\text{II})$  (1), because in the progressive heating of form I at temperatures above  $550^\circ\text{C}$ , a slow generation of the  $\text{CrVO}_4$ -form was observed, without any clear evidence for the presence of another intermediate phase. Nevertheless, this result is in agreement with that of the high-temperature X-ray measurements performed earlier (1).

### Infrared Spectrum

The  $\alpha\text{-MnMoO}_4$  structure is quite complicated and is built up by slightly distorted  $\text{MoO}_4^{2-}$  tetrahedra and highly distorted  $\text{MnO}_6$  octahedra (10). The tetrahedrally coordinated metal ions lie on two different crystal sites; one-half of them on  $C_2$  sites and the remaining ones on  $C_3$  sites.

This structural peculiarity renders it necessary to make a double correlation between the point group of the "free"  $\text{VO}_4^{3-}$  ions ( $T_d$ ) and the site-symmetries in the frame of a "site-symmetry analysis" (12–14), which is presented in Table III. From these results one can see that a large number of IR-active components is expected.

The measured infrared spectrum is shown in Fig. 1; it is evident that a great number of the expected bands must be superimposed, especially in the bending region of the spectrum.

Although the general spectral pattern is quite different from that of the previously

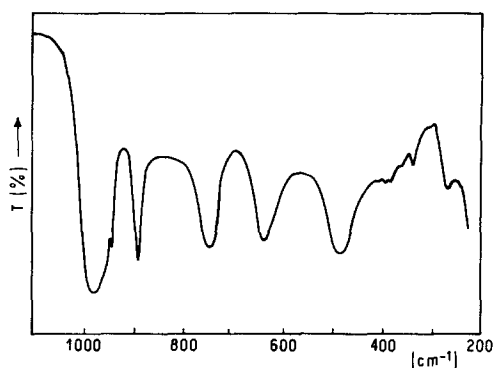


FIG. 1. Infrared spectrum of the low-temperature form of  $\text{InVO}_4$ .

investigated high-temperature form of  $\text{InVO}_4$  (4) the spectral absorption ranges are similar in both polymorphs. In the high-temperature form, the stretching bands are found at 923, 768, and  $723\text{ cm}^{-1}$ . All these bands were assigned to  $\nu_3$  components, whereas the  $\nu_1$  mode, which lies at  $915\text{ cm}^{-1}$  in the Raman effect, is evidently overlapped by the strong  $923\text{-cm}^{-1}$  IR band.

The origin of the large splitting in the  $\nu_3$  region of the high-temperature form, has been explained by the two very different types of V–O distances which are one of the characteristics of the  $\text{VO}_4^{3-}$  units present in the  $\text{CrVO}_4$  structure (cf. also (3, 6, 15)). The results for the presently investigated low-temperature form also point to the presence of one abnormally longer V–O distance into the  $\text{VO}_4^{3-}$  groups.

In the case of  $\alpha\text{-MnMoO}_4$  one of the Mo–O distances is  $1.851\text{ \AA}$ , compared to 1.738, 1.724, and  $1.784\text{ \AA}$  for the three remaining ones (10). As stated in the introduction the infrared spectrum of this compound is very similar to that of Fig. 1; also, the chromates(VI) belonging to this structural type exhibit very similar spectroscopic behavior (6).

Bands located at 982 (with a shoulder at 955), 887, 742 (with a shoulder at 730), and  $634\text{ cm}^{-1}$  can be assigned to the six expected  $\nu_3$  components. The very weak but

TABLE III  
CORRELATION TABLE FOR THE SITE-SYMMETRY ANALYSIS

	"Free" ion ( $T_d$ )	Site-symmetries		Total number of expected IR bands
		$C_2$	$C_3$	
$\nu_1$	$A_1$ (R)	A (IR,R)	$A'$ (IR,R)	2
$\nu_2$	E (R)	2A (IR,R)	$A' + A''$ (IR,R)	4
$\nu_3$	$F_2$ (IR,R)	3A (IR,R)	$2A' + A''$ (IR,R)	6
$\nu_4$	$F_2$ (IR,R)	3A (IR,R)	$2A' + A''$ (IR,R)	6

well-defined  $947\text{-cm}^{-1}$  peak could be one of the predicted  $\nu_1$  modes.

It is interesting that in the case of  $\text{Mg}_3(\text{VO}_4)_2$ , in which considerable splitting is observed in the stretching region (16), one of the V–O distances has a value of ca.  $1.81 \text{ \AA}$ , compared with the mean value of  $1.70 \text{ \AA}$  for the other three V–O bonds (17). In this case, the lowest lying  $\nu_3$  component is located at  $694 \text{ cm}^{-1}$ . This would imply, that in the present case, the longer V–O distance is even higher than in the case of  $\text{Mg}_3(\text{VO}_4)_2$ .

The broad band located at  $484 \text{ cm}^{-1}$  in Fig. 1 can be assigned to an antisymmetric bending vibration. The remaining weaker bands at  $393$ ,  $380$ ,  $338$ , and  $270 \text{ cm}^{-1}$  are probably of a complex origin and involve  $\text{VO}_4$  bendings as well as  $\text{InO}_6$  motions. A similar behavior was found earlier in the case of the structurally related  $\text{MgMoO}_4$  from single-crystal Raman measurements (18). In the case of the  $\text{CrVO}_4$  polymorphs important coupling effects are also detected in the bending region (4, 15).

A comparison of our infrared spectrum with those previously published by Chernysh *et al.* (5) has been made. Our spectrum is practically identical with that of the form called  $\gamma\text{-InVO}_4$  by these authors, which corresponds to a sample obtained at  $600^\circ\text{C}$ . This result is consistent with the findings of Touboul and Ingrain (1) and with our own observations, in the sense that the higher temperature form of  $\text{InVO}_4$  is generated only at temperatures above  $700^\circ\text{C}$ . It thus becomes evident that the Russian authors have not obtained this high-temperature form. On the other hand, it is also intriguing that their X-ray diagrams for the phase obtained at  $600^\circ\text{C}$  is different from either the low- and the high-temperature forms of the material.

Finally, we have also recorded the infrared spectrum of amorphous  $\text{InVO}_4$  samples which show, as expected for such type of materials, very broad and not well-defined

bands. In the stretching region, the main absorption is located at ca.  $815 \text{ cm}^{-1}$  and presents two shoulders at  $900$  and  $720 \text{ cm}^{-1}$ . In the bending region only a medium intensity band centered around  $500 \text{ cm}^{-1}$  is observed. The water absorption bands are found at  $3400 \text{ cm}^{-1}$  (very strong and broad) and at  $1650 \text{ cm}^{-1}$  (medium intensity). The general spectroscopic pattern of this amorphous phase points to a more symmetric vanadium–oxygen environment than those found in the two newly obtained crystalline modifications. In its general form, this spectrum coincides with that published by the Russian authors (5) for an air-dried  $\text{InVO}_4$  specimen.

## Conclusions

The present study clearly demonstrates that the low-temperature form of  $\text{InVO}_4$  obtained by heating the amorphous material generated by precipitation of  $\text{InCl}_3/\text{NH}_4\text{VO}_3$  mixtures at low pH values, is structurally related to  $\alpha\text{-MnMoO}_4$ . It has totally similar crystallographic and vibrational properties as compared to other materials belonging to the same structural type. On the other hand, the amorphous  $\text{InVO}_4$  shows a much simpler infrared spectrum, pointing to a lesser distorted  $\text{VO}_4$  environment, than those which are present in the crystalline phase now characterized or in the previously investigated  $\text{CrVO}_4$  modification.

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