

The Infrared Spectra of the Two Polymorphic Forms of WOPO₄

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The infrared spectra of the two polymorphic forms of WOPO₄ were recorded and assigned by comparison with those of related materials. The results confirm the suspected relation of the high pressure form to that of the tetragonal α -MOPO₄ ($M = \text{Nb, Ta, V, Mo}$) compounds and of the low pressure form with the monoclinic β -NbOPO₄ and β -TaOPO₄. © 1990 Academic Press, Inc.

Introduction

A series of materials of MOPO₄ stoichiometry were characterized in the last years. For $M = \text{Nb}$ a tetragonal form (α -NbOPO₄) has been obtained at low temperatures, whereas a monoclinic modification (β -NbOPO₄) can be prepared at higher temperatures (1-3). In the case of TaOPO₄ a phase transformation from monoclinic to tetragonal occurs under high pressure (3). α -MoOPO₄ and α -VOPO₄ also adopt the tetragonal structure under normal conditions (4-6), whereas β -VOPO₄ presents a different (orthorhombic) structure (6, 7).

Two new materials of this type, containing pentavalent tungsten, could be obtained recently and characterized (8). A low pressure by monoclinic form of WOPO₄ is ap-

parently related to β -NbOPO₄ and β -TaOPO₄, whereas the corresponding high pressure form is tetragonal and should be similar to the α -MOPO₄ phases mentioned above.

In order to obtain a wider insight into the general properties of these new compounds and also to verify spectroscopically the supposed structural relationships with other known materials of this type, we have now analyzed the IR spectra of both forms of WOPO₄.

Experimental

The two polymorphic modifications of WOPO₄ were obtained as previously described (8).

The IR spectra were recorded with a Per-

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kin-Elmer 580 B spectrophotometer, using the KBr pellet technique.

Results and Discussion

The α -WOPO₄ phases possess a layered-tetragonal crystal structure (space group C_{4h}^3 , $Z = 2$). The structure contains distorted WO_6 -groups sharing four equatorial oxygen atoms with four different PO_4 -units. The M atoms are displaced from the center of the WO_6 -octahedra giving one shortened and one elongated $M-O$ bond in the direction of the c -axis of the unit cell (5, 9).

The monoclinic β -WOPO₄ structure (space group C_{2h}^5 , $Z = 8$) is significantly different. Their framework is built up of strands of two WO_6 -octahedra linked with PO_4 -tetrahedra and having pentagonal tunnels, generating a more open structural type than that of the tetragonal form (10, 11). Each WO_6 -octahedron is indeed linked to four PO_4 -tetrahedra which induce four longer $M-O$ distances because of the more covalent character of the phosphorus, compared to the two other $M-O$ distances, which correspond to the corner-sharing WO_6 -octahedra (11).

The IR spectra of both forms are shown in Fig. 1. Band assignments can be made empirically on the basis of previous results for similar materials.

The spectrum of the high pressure form of WOPO₄ closely resembles those of the other tetragonal α -WOPO₄ compounds investigated earlier (9, 12, 13). IR bands at 1180 and 1033 cm^{-1} can be assigned to components of the PO_4 antisymmetric stretching mode. The corresponding symmetric mode is not observed, in agreement with results of a factor group analysis, which shows that this mode belongs to the B_u -symmetry, which is both IR and Raman inactive (13).

The medium intensity band at 930 cm^{-1} can be assigned to the stretching vibration of the shortest $W=O$ bond in the WO_6 -

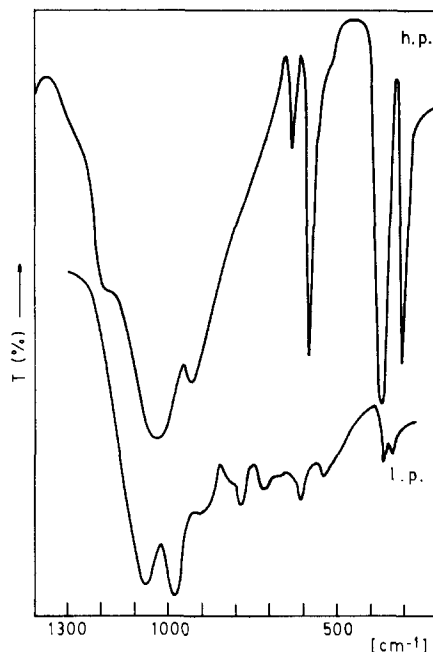


Fig. 1. Infrared spectra of the high-pressure (h.p.) and low pressure (l.p.) forms of WOPO₄.

octahedra. Other stretching modes of these distorted polyhedra are the bands located at 635 and 583 cm^{-1} which, apparently, are strongly coupled with the antisymmetric PO_4 -bendings. The remaining bands (365 and 303 cm^{-1}) are mainly associated to PO_4 -bendings, coupled with WO_6 -deformations.

The stretching of the shorter $W=O$ bond shows practically the same value as that calculated by means of a normal coordinate analysis for $Mo=O$ in α -MoOPO₄ (13) and that found in α -VOPO₄ (9) and it is somewhat higher than that in α -NbOPO₄ (13).

The spectrum of the low pressure form of WOPO₄ although not totally identical, shows some similarities with those of the suspected isostructural phases β -NbOPO₄ and β -TaOPO₄ (14). Two main differences can be pointed out: a distinct intensity

ordering of the three higher energy bands and a poorer definition of the remaining bands in the case of WOPO_4 .

Bands at 1065, 985, and 894 cm^{-1} are assigned to PO_4 -stretching modes. Those at 810 (shoulder), 783, and 720 cm^{-1} are assigned to the W-O stretchings of the shorter WO bonds, i.e., those which share their oxygen atoms with another W atom in each of the pairs of WO_6 -octahedra. On the other hand, bands at 587 and 517 cm^{-1} can, therefore, be assigned to the stretchings of the four longer WO bonds, which share their oxygen atoms with a phosphorus atom. These last modes are probably coupled, to some extent, with OPO deformations. The last doublet (385/357 cm^{-1}) may be also assigned to OPO deformations, but coupled, in this case with WO_6 bendings.

In conclusion, the IR spectrum of the high pressure form of WOPO_4 gives additional support to the suspected close relation of its structure with those of the other tetragonal α - MOPO_4 compounds (8). In the case of the low pressure form although the spectrum is not totally similar to that of the monoclinic forms of TaOPO_4 and NbOPO_4 , its general characteristics point also to a structural relationship with these materials.

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