

## Pressure-induced structural transitions and valence change in $\text{TlReO}_4$ : A high-pressure Raman study

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The pressure dependence of the Raman-active vibrational modes in  $\text{TlReO}_4$  has been investigated up to 16 GPa, using the diamond-anvil cell. The abrupt changes in the Raman spectra indicate that three pressure-induced phase transitions occur at 0.5, 1.9, and 9.7 GPa. The first two transitions are not accompanied by any significant change in the optical characteristics of the sample, but in the third transition—at 9.7 GPa—the sample turns black, exhibiting a deep red transmission in the very thin edges, revealing that it is still an insulator. The transition to phase II, we believe, is subtle and probably involves a doubling of a crystal axis, while phase III is likely to have the same structure as  $\text{LiReO}_4$ . From the large shift (more than 2 eV) in the optical absorption at the III-to-IV transition and from the absence of such a change in  $\text{KReO}_4$  up to 25 GPa, we propose that the latter transition in  $\text{TlReO}_4$  involves a change in the valence state of Tl to the  $\text{Tl}^{3+}$  state and that of Re to  $\text{Re}^{5+}$  to maintain charge neutrality. The latter valence states are known for Tl and Re. Phase IV is a low-symmetry structure, and apparently the change in the ionic size triggers the structural transition. The change in the optical characteristics of phase IV suggests the possibility of a metallic state for  $\text{TlReO}_4$  in the pressure range 20–30 GPa.

### INTRODUCTION

The influence of pressure on the structural stability of a number of  $\text{ABO}_4$  tungstates and molybdates crystallizing in the scheelite structure has recently been investigated by Raman spectroscopy.<sup>1,2</sup> These studies have revealed that pressure-induced phase transitions are ubiquitous in them. There is a series of perrehenates of the type- $A$   $\text{ReO}_4$  where  $A$  is an alkali metal, ammonium, or Tl, and these crystallize in the scheelite or the pseudoscheelite structure.<sup>3</sup> These compounds are of interest, for they may be expected to undergo similar pressure-induced phase changes. Among these the  $\text{TlReO}_4$  is particularly interesting because of the possibility of a pressure-induced valence change in Tl to the  $\text{Tl}^{3+}$  state.

Therefore, in this study we have investigated  $\text{TlReO}_4$ , which crystallizes in the pseudoscheelite structure with orthorhombic symmetry.<sup>3</sup> We observe three pressure-induced phase transitions in the interval 0.1–16 GPa. Among these, the first two phase transitions which occur near 0.5 and 2.0 GPa, respectively, are purely structural and, further, do not exhibit any visible changes in the optical characteristics of the sample. However, the third phase transition near 10 GPa is accompanied by a striking change in color; the colorless transparent sample turns black, exhibiting a deep red transmission only in very thin portions, and at  $\sim 15$  GPa it becomes totally opaque in the visible. This change indicates a drastic modification in the electronic structure and we believe that this transition is caused by a change in the valence state of Tl to the  $\text{Tl}^{3+}$  state and that of Re to  $\text{Re}^{5+}$ . The results of these studies will be presented and discussed in this paper.

### EXPERIMENTS AND RESULTS

High pressure was generated in a gasketed diamond-anvil cell<sup>4</sup> with 4:1 methanol-ethanol mixture, as well as argon as pressure medium. Pressure was calibrated by the well-known ruby fluorescence technique.<sup>5</sup> Samples for high-pressure Raman study were from a single-crystal specimen which was colorless and transparent. Small crystal fragments (50–100  $\mu\text{m}$  in linear dimension and about 20–50  $\mu\text{m}$  in thickness) were mounted in the cell. For optical-absorption studies samples which had a plateletlike geometry were chosen.

Raman spectra in the diamond cell were recorded in the backscattering geometry using a Spex double monochromator equipped with a conventional photon-counting system. For excitation the 488-nm laser line from an argon-ion laser was used at a power level of 20–30 mW. In phase IV (at pressures above 9.7 GPa) the 647.1-nm line from a  $\text{Kr}^+$  laser had to be employed, since the sample became opaque to 488- or 514.5-nm lines of the  $\text{Ar}^+$  laser. Only qualitative absorption measurements were made, using the setup which has been previously described.<sup>1</sup> All the spectra were recorded at room temperature.

Figures 1 and 2 show the Raman spectrum of  $\text{TlReO}_4$  taken at four different pressures. From these spectra and from Figs. 3–5, it is clear that pressure-induced phase transitions occur at pressures near 0.5, 1.9, and 9.7 GPa. The Raman spectra of phases III, II, and I are shown in Fig. 1 and the spectrum of phase IV is shown in Fig. 2. In the spectra shown in Fig. 1 the Raman peaks fall under three distinct sets of bands, which lie, respectively, in the regions 20–100  $\text{cm}^{-1}$ , 300–400

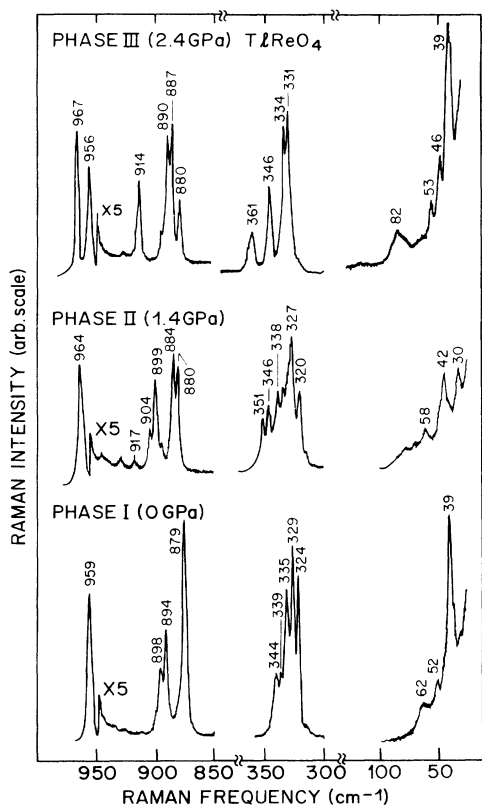


FIG. 1. Raman spectra of  $\text{TiReO}_4$  at three different pressures corresponding to three different phases. Spectra were taken with 488-nm excitation at a power level of 30 mW.

$\text{cm}^{-1}$ , and 850–1000  $\text{cm}^{-1}$ . The peaks in the first band arise from the external modes of the crystal, while the peaks in the latter two bands are the internal vibrational modes of the  $\text{ReO}_4^-$  ion. In Fig. 2 similar vibrational modes exist, except for the presence of additional weak Raman peaks in the gap regions. A comparison of the detailed features in the spectra reveal that the difference between phases I and II is subtle. Several of the mode frequencies split in phase II, revealing that phase II has a lower symmetry. The highest-frequency mode represents the stretching vibrational frequency of the Re—O bond and this mode splits up in phase III and phase IV. Phase IV is very rich in Raman peaks and

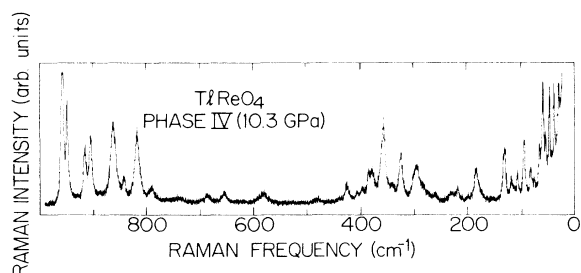


FIG. 2. Raman spectrum of  $\text{TiReO}_4$  at 10.3 GPa corresponding to phase IV. The 647.1-nm  $\text{Kr}^+$  laser line was used for excitation at a power level of 30 mW.

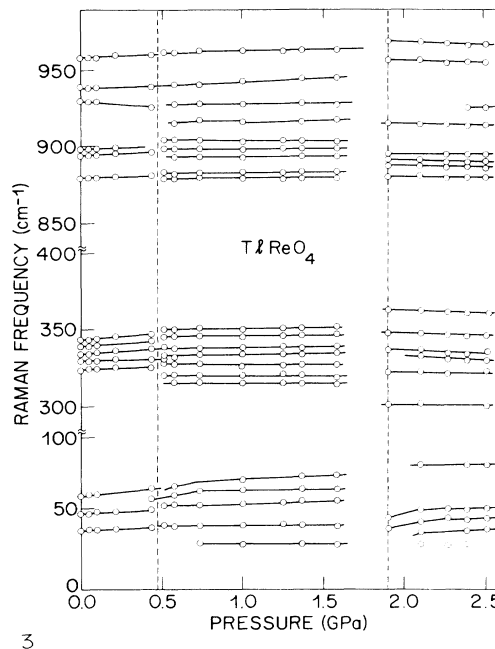


FIG. 3. Pressure dependence of the Raman active modes of  $\text{TiReO}_4$  plotted up to 2.5 GPa. The dashed lines near 0.5 and 2.0 GPa delineate the first two phase transitions. The restricted pressure range brings out the first two transitions clearly.

from this we believe that it must be a very low-symmetry structure. An interesting observation is that we see no observable change in the optical characteristics of the sample, when viewed through a high power microscope, in going from phase I to II and again from phase II to

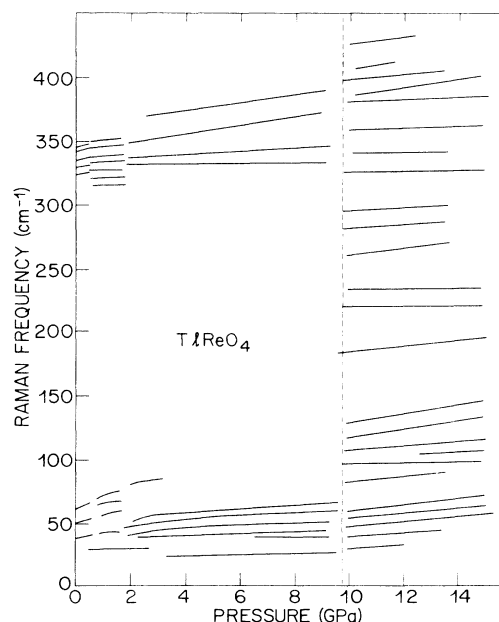


FIG. 4. Pressure dependence of the Raman active modes of  $\text{TiReO}_4$  in the 0–450- $\text{cm}^{-1}$  frequency region over the full range of pressures investigated. The dashed line at 9.7 GPa marks the pressure at which the third phase transition occurs. The first two transitions appear very compressed.

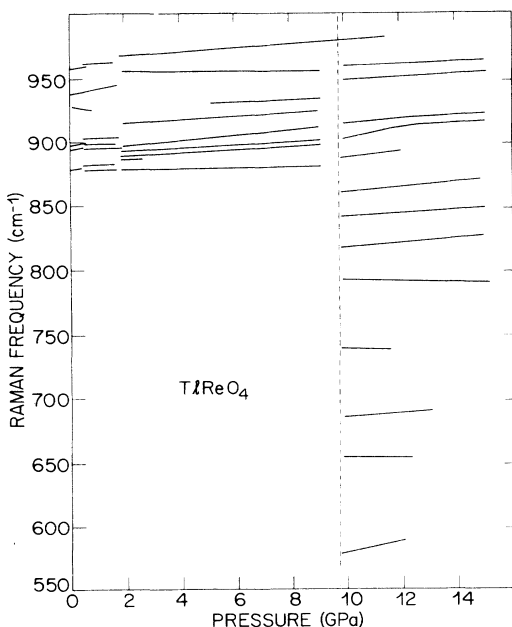


FIG. 5. Pressure dependence of the Raman active modes of  $\text{TiReO}_4$  in the  $550\text{--}1000\text{-cm}^{-1}$  frequency region over the full range of pressures investigated. The dashed line at 9.7 GPa marks the pressure at which the third phase transition occurs.

III. However, in the III-to-IV transition the sample abruptly turns black, exhibiting a deep red transmission only at the very thin edges. Hence, to record the Raman spectrum of phase IV we had to use the  $647.1\text{-nm}$  line of a  $\text{Kr}^+$  laser.

In Fig. 3 the pressure dependence of the observed Raman peaks are shown for the lower-pressure region. The phase-transition pressures are indicated by the dashed vertical lines. In Figs. 4 and 5 this pressure dependence is shown over the entire range of pressure investigated wherein the low-pressure region appears very much compressed. The data points have been omitted for the sake of clarity and the phase III-to-IV phase transition is indicated by the dashed line. The Raman peaks change abruptly at all the above phase transitions, from which we conclude that they must be first-order transitions. In Table I the observed Raman mode frequencies are listed for the four phases, at pressures close to those labeled in the spectra shown in Figs. 1 and 2.

## DISCUSSIONS

The perrehanates involving monovalent cations crystallize in the scheelite structure,<sup>3</sup> with the exception of  $\text{LiReO}_4$ ,  $\text{CsReO}_4$ , and  $\text{TiReO}_4$ . Among these the latter two have the pseudoscheelite structure with orthorhombic symmetry<sup>3</sup> and belong to the space group  $D_{2h}^{16}$ , with four molecules in the unit cell. The crystal structure of the Li compound is not known. The Raman and infrared spectra of these compounds have been reported<sup>3</sup> and, for  $\text{NH}_4\text{ReO}_4$ ,<sup>6</sup> even a high-pressure Raman study<sup>7</sup> has been carried out to 1.6 GPa.

A rather simplifying aspect of the vibrational spec-

trum of the monovalent perrehanates is the clear separation of the vibrational modes of the  $\text{ReO}_4^-$  group from that of the lattice vibrational modes. The former in general lie at high frequencies and the latter are in the low-frequency range. A group-theoretical analysis for the vibrational modes of the  $\text{ReO}_4^-$  ion in the scheelite structure ( $C_{4h}^6$ ) yields seven internal Raman-active modes (for the factor group  $C_{4h}$ ) which are the stretching  $\nu_1 (A_g)$ ,  $\nu_3 (B_g)$ , and  $\nu_3 (E_g)$ ; bending  $\nu_2 (A_g)$ ,  $\nu_2 (B_g)$ ,  $\nu_4 (B_g)$ , and  $\nu_4 (E_g)$ . For the pseudoscheelite structure the space group is  $D_{2h}^{16}$  ( $Pnma$ ) and the factor group is  $D_{2h}$ . This results in the doubling of the above seven modes.<sup>3</sup> Further there are a number of external Raman-active modes.

In an earlier study on  $\text{TiReO}_4$  two external mode peaks and eight internal mode peaks have been reported.<sup>3</sup> In the present study three external mode peaks and eleven internal mode peaks are observed. These are listed in Table I under phase I and reproduced in the bottom spectrum of Fig. 1. A few very weak and broad peaks are observed (marked with asterisks) and they are believed to be combination modes or second-order scattering.

An examination of the spectrum of phase II (see Fig. 1 center spectrum) reveals that some of the peaks of phase I are doubled. This is particularly well seen in the peaks lying in the regions  $300\text{--}350\text{ cm}^{-1}$  and  $850\text{--}900\text{ cm}^{-1}$ . The three weak Raman peaks between  $910$  and  $950\text{ cm}^{-1}$  are believed to be second order or combination bands. We attribute the doubling of several Raman peaks in phase II to a doubling of the unit cell along a crystallographic direction, resulting in the folding of several zone-boundary phonons into the zone center. The transition from phase I to phase II occurs around 0.5 GPa and is first order. However, no change in the optical properties is observed. We believe that this transition involves no major structural change, except perhaps a rotation or tilt of the  $\text{ReO}_4$  polyhedra. Polyhedral tilt transitions induced by pressure are well known.<sup>8</sup>

The II-to-III phase transition occurs near 2 GPa and is accompanied by further changes in the Raman spectrum. The striking change is the splitting of the  $\nu_1$  stretching frequency of the  $\text{ReO}_4^-$  polyhedra into two components with more or less equal intensity. The Raman spectrum of phase III is strikingly similar to the spectrum of  $\text{LiReO}_4$ . Therefore, we believe that the structure of phase III may be the same as that of  $\text{LiReO}_4$ . The crystal structure of  $\text{LiReO}_4$  is not known but Ulbricht and Kriegsmann<sup>3</sup> assume it to be of the wolframite-type (monoclinic symmetry) and have interpreted their Raman and infrared spectrum on that basis. A transition from scheelite or pseudoscheelite to wolframite structure would be consistent for the  $\text{ABO}_4$  compounds, from packing efficiency considerations.

The pressure-induced phase transition from phase III to phase IV near 10 GPa is followed by striking changes both in the Raman spectrum as well as the color of the sample. The latter abruptly turns black. However, the sample exhibits a deep red transmission along the very thin edges revealing thereby that it is still an insulator.

TABLE I. Observed Raman peaks in the pressure-induced polymorphs of  $\text{TlReO}_4$ . vs is very strong; s is strong; m is medium; w is weak; vw is very weak.

Phase I (0.1 GPa) $\omega$ ( $\text{cm}^{-1}$ )	Phase II (1 GPa) $\omega$ ( $\text{cm}^{-1}$ )	Phase III (2.4 GPa) $\omega$ ( $\text{cm}^{-1}$ )	Phase IV (10.3 GPa) $\omega$ ( $\text{cm}^{-1}$ )
Lattice mode frequencies at $\text{ReO}_4^-$			
39s	29s	39s	30s
49w	42s		38s
			48s
			56m
62w <sup>a</sup>	56w	46m	61s
			67m
	65vw <sup>a</sup>	53m	83m
			95m
	72vw <sup>a</sup>		
			118w
			131m
			184m
Internal mode frequencies of $\text{ReO}_4^-$			
			294m
324s	320m	331s	324m
	327s		357s
329s		334s	
	334m		379m
335s		346m	385m
	338m		397w
339m		361m	
	345m		407w
344m	350m		426m
879s	879s	880m	790w
894m	883s	887s	817s
898m	893w	890s	842w
	898s	895w	826s
959vs	903w	914s	904s
	963vs	956vs	914m
			948s
		967vs	957s

<sup>a</sup>Probably second order or combination bands.

For phase IV, numerous Raman peaks appear in the external and internal mode regions and the richness of the spectrum indicates a further lowering of symmetry.

As mentioned above a remarkable feature of the III-to-IV phase transition is the change in the optical absorption. We made some semiquantitative absorption edge measurements to obtain a rough estimate of the shift in the energy gap across the transition, and found that the gap decreased by about 2 eV in phase IV. This large shift must involve a major change in the electronic band structure of  $\text{TlReO}_4$  at about 10 GPa. At pressures near 15 GPa the sample became totally black. Neither Raman nor absorption data could be recorded at this pressure with our setup. Further, we find that in the case of  $\text{KReO}_4$ , another rhenate that we have studied under high pressure,<sup>9</sup> no striking change in the optical absorption is observed up to 25 GPa, although two or possibly three phase transitions are encountered. Therefore we believe that the III-to-IV transition in  $\text{TlReO}_4$  involves a charge transfer from Tl to Re in which the electronic configuration change  $\text{Tl}^{1+}(\text{Re}^{7+}\text{O}_4)^{-1} \rightarrow \text{Tl}^{3+}(\text{Re}^{5+}\text{O}_4)^{-3}$  takes place. Both the trivalent state

of Tl and the pentavalent state of Re are known.<sup>10</sup> In the crystal this must involve a charge transfer from the Tl-derived bands into the Re bands. Evidently this electronic instability triggers a structural phase transition, for the size of the ions changes when the valence state changes. A high-pressure x-ray diffraction study would be instructive and this is in progress.

It is worth noting here that the phase transitions in  $\text{TlReO}_4$  are completely reversible on release of pressure, but a large hysteresis is observed; the IV-to-III phase transition occurs near 5.9 GPa, the III-to-II phase transition near 1.1 GPa, and the II-to-I phase transition near 0.4 GPa on releasing pressure. The hysteretic aspect is strong evidence for the first-order nature of the phase transitions.

#### SUMMARY AND CONCLUSIONS

(1) From the changes in the Raman spectra we find three pressure-induced phase transitions in  $\text{TlReO}_4$  at 0.5, 2, and 10 GPa. The first two transitions do not show any visible changes in the optical characteristics,

but the third transition is accompanied by a striking change in the optical transmission. The sample turns practically opaque to the visible radiation.

(2) The detailed features in the Raman spectra is indicative of a subtle phase transition at 0.5 GPa, probably involving a doubling of a crystallographic axis, whereas the 2-GPa transition appears to be due to a transformation of phase II to the  $\text{LiReO}_4$  structure, which is presumed to be of the wolframite type.

(3) The absorption edge shift at the III-to-IV phase transition indicates a drastic change in the electronic structure. For this we propose a change in the valence state of Tl from  $\text{Tl}^{1+}$  to the  $\text{Tl}^{3+}$  state and of Re from  $\text{Re}^{7+}$  to the  $\text{Re}^{5+}$  state to maintain charge neutrality. This valence change must involve a charge transfer from Tl derived bands to the Re bands in the crystal. We be-

lieve that this electronic change triggers the structural transition III to IV. A high-pressure Mössbauer or LIII absorption edge studies may be expected to elucidate further the nature of the above novel aspect of the III to IV phase transition.

(4) From the rapid change in the optical absorption, we suggest that  $\text{TlReO}_4$  would turn metallic in the 20–30-GPa range. Whether the metallic phase would exhibit superconductivity is an interesting question and possibility.

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