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Temperature-induced phase transitions in $TlReO_4$: A Raman spectroscopic and x-ray diffraction study

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Temperature-induced phase transitions in $TlReO_4$ have been investigated by Raman spectroscopy and by x-ray powder diffraction. The data reveal the occurrence of a hitherto unreported phase transition from orthorhombic to the tetragonal scheelite-type structure near 200 K and this is a first-order transition. At temperatures above 400 K the orthorhombic phase is known to transform to the scheelite-type structure. These phase changes present a unique situation. The lattice parameters of the low-temperature (LT) scheelite phase are $a_0 = 5.798$ Å and $c_0 = 12.920$ Å at 70 K and for the tetragonal high-temperature (HT) scheelite phase are $a_0 = 5.761$ Å, and $c_0 = 13.33$ Å at 400 K. The corresponding unit-cell volumes are 434 Å^3 and 442 Å^3. For the orthorhombic phase $a_0 = 5.623$, $b_0 = 5.791$, $c_0 = 13.295$, and $V = 432$ Å^3 at 293 K. The orthorhombic–LT-scheelite and the orthorhombic–HT-scheelite phase boundaries drawn on the basis of the ΔV's at the transition point intersect at negative pressures in a P-T diagram. This intersection appears to satisfy the criteria required for the occurrence of an "isolated point" in the P-T plane; namely a point at which two first-order phase boundaries intersect to become a continuous transition. This is probably the first experimental indication for such a possibility.

INTRODUCTION

The perrhenates of alkali metals, NH_4 and Tl crystallize in the tetragonal (scheelite) or the related orthorhombic (pseudoscheelite) structure[1] with the exception of $LiReO_4$ whose structure is unknown. Detailed Raman studies[2] have been carried out on them and the observed vibrational models have been identified with the expected internal and external modes of the crystal. High-temperature x-ray diffraction studies have shown that Tl and Cs perrhenates undergo a temperature-induced phase transition[1,3] from the orthorhombic to the tetragonal lattice near 400 K.

We recently investigated the effect of high pressure[4] on $TlReO_4$ using Raman scattering as a probe and have found that it undergoes three pressure-induced phase transformations in the interval 0.1–16 GPa. Since the first pressure-induced phase transition occurred at a low pressure of 0.5 GPa, we felt that this transition boundary might intersect the pressure axis at some low temperature. This possibility motivated us to study the temperature dependence of the Raman spectrum of $TlReO_4$ down to liquid-nitrogen temperature at ambient pressure. We have also carried out a low-temperature x-ray powder diffraction study to explore the crystal structure of $TlReO_4$ down to liquid-N_2 temperatures. Our study reveals a hitherto unreported phase transition near 200 K, but the low-temperature phase turns out to be different from the pressure-induced phase near 0.5 GPa. Quite surprisingly the low-temperature phase also has the tetragonal scheelite-type structure, just as at temperatures above 400 K. The x-ray diffraction and Raman studies clearly establish this unique situation where the orthorhombic (pseudoscheelite) phase appears as an intruder. The results of these studies and their implications will be presented and discussed in this paper.

EXPERIMENTS AND RESULTS

A small crystal of $TlReO_4$ was attached to the copper block of a homemade glass optical cryostat which was cooled with liquid nitrogen. Raman spectra were taken while the sample was slowly warming from 77 K upwards. Temperature was measured with a Chromel-Alumel thermocouple placed close to the sample. The cryostat was kept under continuous evacuation, with the pressure near 5×10^{-6} Torr. For temperatures above 290 K, the sample was attached to a copper rod which was heated with two ceramic resistors. The current to the resistors was controlled with a Variac. Again, the temperature was measured with a Chromel-Alumel thermocouple. In this case the whole setup was open to the atmosphere.

Raman spectra were taken with a Spex double monochromator equipped with a conventional photon-counting system. For excitation the 488-nm line from an Ar^+ laser was used at power levels of 20 mW. In Fig. 1 the Raman spectra of $TlReO_4$ are shown at 90, 273, and 435 K. It is evident that the spectra are different; the 273-K spectrum is for the orthorhombic phase, the 435-K spectrum is for the high-temperature (HT) tetragonal phase, and the 90-K spectrum is for the low-temperature (LT) tetragonal phase. The orthorhombic phase transforms to the HT tetragonal (scheelite) phase at 400 K on heating, and to the LT tetragonal (scheelite) phase near 200 K. The temperature dependence of the Raman peak frequencies are plotted in Fig. 2 when the vertical dashed lines mark the phase-transition temperatures. The phase transitions are found to be readily reversible and are first order.

Low-temperature x-ray powder diffraction studies were performed with a closed-cycle helium refrigerator. The powdered sample was dispersed on a platinum substrate and sealed in a He-filled chamber. To minimize scattering from the cryostat windows, a "three-crystal" geometry

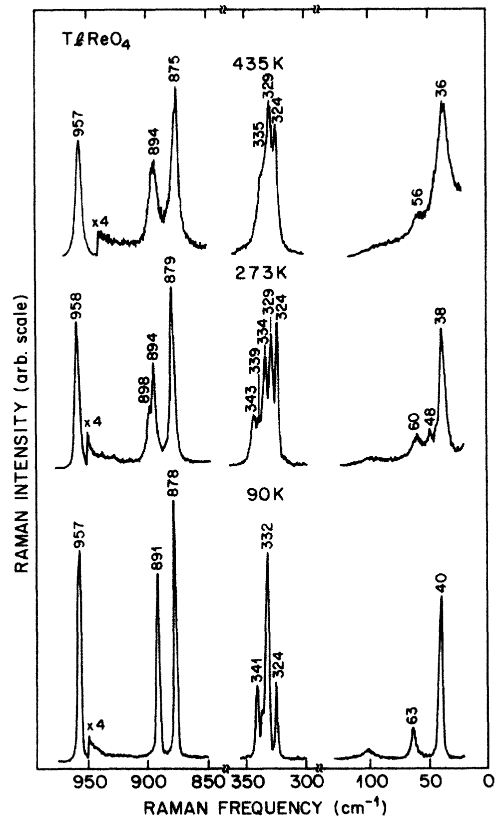

FIG. 1. The Raman spectrum of $TlReO_4$ at 90, 273, and 435 K. The structure of $TlReO_4$ at 90 and 435 K is tetragonal (scheelite-type) and at 273 K orthorhombic (pseudoscheelite). The 435-K spectrum is the broadened version of the 90-K spectrum.

consisting of a pyrolytic graphite (PG) monochromator, the sample, and a PG analyzer was used. The x-ray powder diffraction data obtained on the LT phase at 70 K are presented in Table I and the pattern has been indexed on the basis of a tetragonal cell with $a_0 = 5.798 \pm 0.005$ Å and $c_0 = 12.920 \pm 0.005$ Å. The unit-cell volume is obtained as 434.4 Å^3.

DISCUSSION

Earlier x-ray diffraction studies[3] have established that the perchlorates, technetates, and rhenates of Tl and Cs, which crystallize in the orthorhombic structure (D_{2h}^{16}-P_{nma}), transform at higher temperature to a cubic (in the case of perchlorates), or to the tetragonal scheelite structure (in the case of rhenates and technetates). The technetium compounds appear to have a lower transition temperature compared to the rhenium compounds. A nuclear quadrupole resonance study[5] of $TlReO_4$ at low temperatures has shown that a change in the asymmetry parameter η occurs at $T < 200$ K indicating some kind of phase transition to a higher symmetry; η appears to go to zero. The present Raman study provides definitive evidence for a change of structure to the tetragonal scheelite phase at 203 K.

Group theory predicts 14 Raman active vibrations for the internal modes of the ReO_4 group and six external

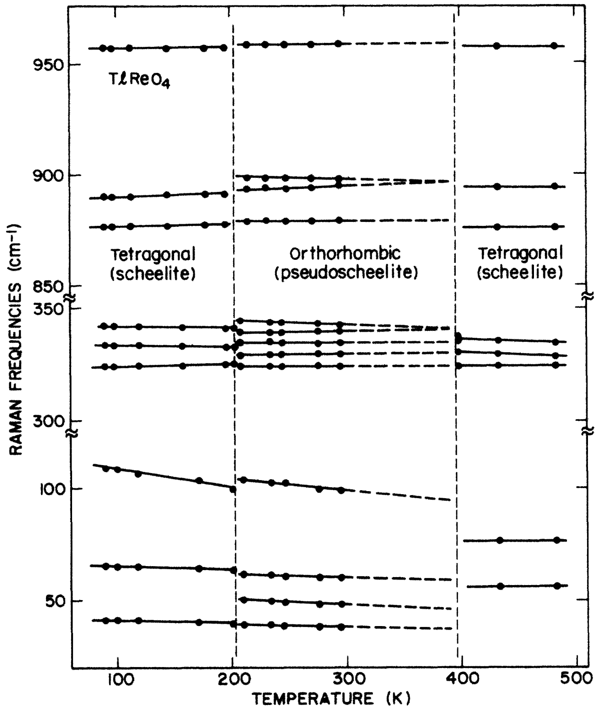

FIG. 2. The temperature dependence of the phonon frequencies and the temperature-induced phase transitions. At temperature above 400 K and below 203 K the orthorhombic (pseudoscheelite) $TlReO_4$ transforms to the tetragonal (scheelite-type) lattice.

TABLE I. X-ray diffraction data on the low-temperature tetragonal phase of $TlReO_4$. $T = 70$ K, $a_0 = 5.798$ Å and $c_0 = 12.919$ Å. vs denotes very strong; s, strong; m, medium; wm, weak medium; and w, weak.

d observed (Å)	Intensity	*hkl*
3.472	vs	112
3.242	s	004
2.904	s	200
2.539	w	114
2.158	s	204
2.050	m	220
1.905	s	116
1.763	s	312 (303)
1.730	s	224
1.614	m	008
1.449	w	400
1.410	m	208
1.396	m	316
1.337	m	332 (413)
1.322	wm	404
1.297	wm	420
1.268	m	228
1.232	m	1,1,10
1.203	m	424
1.153	m	336
1.120	m	512 (433,503)
1.077	wm	408 (0,0,12)
1.055	wm	3,1,10
1.009	m	2,0,12

TABLE II. Crystallographic data of the three phases of $TlReO_4$ and their unit-cell volumes for the HT-tetragonal phase at 400 K, the LT-tetragonal phase at 70 K, and the orthorhombic phase at 293 K. The volume change ΔV of 7 ± 2 Å^3 for the orthorhombic to the HT-tetragonal phase, and 8 ± 2 Å^3 for the orthorhombic to the LT-tetragonal phase were obtained at the respective transition temperature, namely, 400 and 200 K, after correcting the volumes given in the table above for the thermal expansion or contraction as the case may be.

HT tetragonal[a]		Orthorhombic[a]		LT tetragonal
(Scheelite-type) C_{4h}^6	⇆ 400 K	(Pseudoscheelite) D_{2h}^{16}	⇄ 803 K	(Scheelite-type) C_{4h}^6
$a_0 = 5.761 \pm 0.005$ Å $c_0 = 13.33 \pm 0.01$ Å		$a_0 = 5.623 \pm 0.005$ Å $b_0 = 5.791 \pm 0.005$ Å $c_0 = 13.295 \pm 0.005$ Å		$a_0 = 5.798 \pm 0.005$ Å $c_0 = 12.919 \pm 0.005$ Å
$V = 442$ Å^3		$V = 432$ Å^3		$V = 434$ Å^3
	$\Delta V = 7 \pm 2$ Å^3		$\Delta V = 8 \pm 2$ Å^3	

[a] Data from Ref. 1.

modes (lattice modes) for the orthorhombic phase of $TlReO_4$. For the tetragonal phase of $TlReO_4$ (C_{4h}^6) seven internal modes and six external modes are predicted. The Raman spectrum of $TlReO_4$ at temperatures above 400 K is consistent with the spectrum expected for the higher-symmetry scheelite-type tetragonal lattice. The Raman peaks are somewhat broader, and this is to be expected at higher temperature. This transition has been located at 400 ± 5 K by differential thermal analysis[3] (DTA) and by high-temperature x-ray powder diffraction.[1] The Raman spectrum taken below 200 K is identical with that of the HT scheelite phase except the peaks are sharper and slightly higher in frequency, which is to be expected at low temperatures. Our low-temperature x-ray powder diffraction data confirm that the low-temperature phase has also the tetragonal scheelite-type structure. In Table II the crystallographic data and the unit-cell volume are presented. We have a rather unique situation in $TlReO_4$ where the tetragonal scheelite phase is stable above 400 K and then below 200 K, with the orthorhombic phase as the intruder.

From the unit-cell volumes it can be inferred that the orthohormbic-HT-tetragonal phase boundary should have a positive dT/dP. That this is a first-order line is proven by the thermal arrest DTA signals[3] obtained in crossing the line. As for the orthorhombic-LT-tetragonal boundary, a negative slope is indicated by the volume change at the transition (see Table II). We believe that this is also a first-order line because strains and fractures develop in the optically clear samples, when crossing the line. From the indicated slopes a P-T diagram has been drawn and is presented in Fig. 3. The two first-order lines would intersect on the negative pressure side as shown. Now the interesting question is, what is the nature of the point at the intersection. If another first-order boundary meets it from the left side, it would obviously be a commonly occurring triple point in the P-T plane. However, in the present case the tetragonal scheelite phase would be the only phase to the left of the point and it should be a continuous transition from the LT- to the HT-tetragonal phase, if one can call it a transition. But, this side of the P-T diagram is inaccessible for experimentation because it is at negative pressure. At the moment it is not clear to us as to what could be the physical difference between the LT- and HT-tetragonal phase. The Raman spectra of the two phases are identical and the x-ray data confirm that they have the same structure.

Landau and Lifshitz[6] have given a detailed discussion of the intersection of phase boundaries of different kinds. According to them a continuous phase transition can occur at "isolated points" if there is only one invariant of third order in the expansion of the thermodynamic potential. These points should lie at the intersections of curves (in the P-T plane) of first-order phase transitions. Thus it seems possible from their arguments that two first-order phase lines could intersect to give a point, beyond which only a continuous transition occurs, provided two phases have the same symmetry and the third phase a different symmetry. The hypothetical phase diagram presented in Fig. 3 appears to qualify these criteria. The LT- and HT-tetragonal phases have certainly the same symmetry, while the pseudoscheelite has the orthorhombic symmetry. Since there is no symmetry restriction it is possible to go continuously from the LT-tetragonal to the HT-

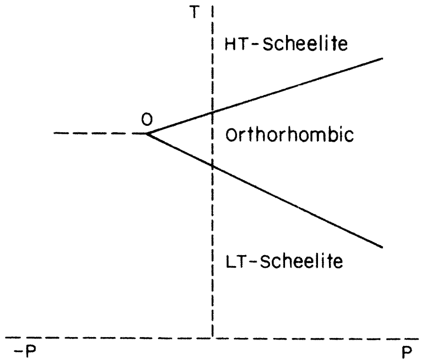

FIG. 3. The P-T diagram showing the orthorhombic to HT-tetragonal and the orthorhombic to LT-tetragonal phase boundaries. The slopes are arbitrary but the signs of the dT/dP are fixed from the ΔV accompanying the transition.

tetragonal phase, left of the point of intersection. Landau and Lifshitz comment that isolated continuous transition points have not yet been observed experimentally.[6] The system $TlReO_4$ seems to be a case in which this possibility could be realized, although the isolated point occurs on the negative pressure side. Perhaps, with some suitable dopant this might be shifted to positive pressure, thus becoming accessible to experimentation.

SUMMARY AND CONCLUSIONS

Thallium perrhenate ($TlReO_4$) exhibits two temperature-induced phase transitions at ambient pressure, from the orthorhombic to a tetragonal scheelite-type lattice. The orthorhombic phase is stable between 400 and 200 K. Above 400 K it transforms to a HT-tetragonal phase which has the scheelite-type lattice. Similarly the orthorhombic phase transforms to a LT-tetragonal phase, again of the scheelite type below 200 K. Both high-pressure x-ray diffraction and Raman studies are consistent with regard to this interpretation. We have a rather unique situation with $TlReO_4$. A *P-T* diagram has been proposed which indicates the termination of two first-order phase boundaries at an intersection, which seems to qualify for the "isolated point" discussed by Landau and Lifshitz, hitherto unobserved experimentally.

In this connection the perchlorates and technetates of Tl and Cs become very interesting systems for future investigations. Also, the effect of doping with other alkali-metal ions such as Cs, Rb, and K on the structural properties of $TlReO_4$ may be revealing.

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