

A high pressure Raman study of TeO₂ to 30 GPa and pressure-induced phase changes

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MS received 10 August 1990

Abstract. The effect of pressure on the Raman modes in TeO₂ (paratellurite) has been investigated to 30 GPa, using the diamond cell and argon as pressure medium. The pressure dependence of the Raman modes indicates four pressure-induced phase transitions near 1 GPa, 4.5 GPa, 11 GPa and 22 GPa. Of these the first is the well studied second-order transition from D_4^+ symmetry to D_2^+ symmetry, driven by a soft acoustic shear mode instability. The remarkable similarity in the Raman spectra of phases I to IV suggest that only subtle changes in the structure are involved in these phase transitions. The totally different Raman spectral features of phase V indicate major structural changes at the 22 GPa transition. It is suggested that this high pressure-phase is similar to PbCl₂-type, from high pressure crystal chemical considerations. The need for a high pressure X-ray diffraction study on TeO₂ is emphasized, to unravel the structure of the various high pressure phases in the system.

Keywords. Raman spectroscopy; high pressure; diamond anvil cell; phase transition.

PACS Nos 64.70; 62.50; 78.30

1. Introduction

Tellurium dioxide (TeO₂) is known to crystallize in three different structures at ambient pressure (Wyckoff 1963); an orthorhombic phase of D_{2h}^{15} symmetry and two tetragonal structures of symmetry D_{4h}^{15} (rutile structure) and D_4^+ (paratellurite). Large single crystals of excellent quality have been grown in the paratellurite phase and the material is of interest for piezoelectric and electrooptic applications.

Ultrasonic, dielectric, Raman, Far-IR and Brillouin scattering studies on paratellurite under high pressure have been reported (Percy *et al* 1975; Adams and Sharma 1978). From high pressure studies the occurrence of a second-order pressure-induced phase transition in paratellurite near 1 GPa has been established and it has been shown that the transition is driven by a soft acoustic shear mode instability (Percy *et al* 1975). The suggestion that the high pressure phase should possess orthorhombic D_2 symmetry has been verified by high pressure neutron studies (Worlton and Beyerlein 1975). At the phase transition neither a discontinuous volume change nor a change in the number of atoms in the unit cell occurs, supporting the second-order nature of the transition. The Raman and Far-IR study to 4.5 GPa (Adams and Sharma 1978) has confirmed these results but could not find the 3 GPa transition claimed by Kabalkina *et al* (1967).

From a high pressure X-ray diffraction study on TeO₂, Ming and Manghnani

(1982) have reported a phase transition from the orthorhombic D_2 phase to another orthorhombic phase near 12 GPa. They suggested the $PbCl_2$ structure for the new high pressure phase. The occurrence of this transition has been questioned by Liu (1987). The latter author has concluded from his high pressure X-ray diffraction studies on paratellurite that no phase transition occurs in TeO_2 up to 25 GPa, other than the one from D_4^4 to D_2 near 1 GPa.

As a part of our program on high pressure Raman studies of oxides we have investigated TeO_2 (paratellurite) to 30 GPa by Raman scattering. We find evidence for four pressure-induced phase transitions in the pressure range 0 to 30 GPa. The results of this study will be presented and discussed in this paper.

2. Experiments and results

A large single crystal of paratellurite of very fine optical quality grown in our laboratories were available to us and samples for the high pressure study were splintered from the large boule.

High pressure Raman scattering experiments were carried out using a gasketed diamond anvil cell of the Mao-Bell type (Jayaraman 1983). In our experiments argon was used as pressure medium, since Adams and Sharma (1978) have commented in their paper that TeO_2 reacts with the conventionally used 4:1 methanol-ethanol mixture. Pressure was calibrated by the well-known ruby fluorescence technique (Barnett *et al* 1973). 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 30–60 mW. All the spectra were recorded at room temperature.

The Raman spectra obtained at five different pressures are shown in figure 1. The ambient pressure spectrum (marked 0 GPa) is that of the paratellurite phase. In table 1 the observed Raman peaks are listed along with the symmetry designation of the mode, following Adams and Sharma (1978). The pressure dependence of the Raman peaks are shown in figures 2 and 3 for the lower and higher frequency regions respectively. From the abrupt changes in the pressure dependence of the Raman peaks we believe that four pressure-induced phase transitions occur in TeO_2 in the 0 to 30 GPa range; the first transition near 1 GPa, the second near 4.5 GPa, the third near 11 GPa and a fourth transition near 22 GPa. The five Raman spectra presented in figure 1, we believe, are the representative spectra of the five phases I to V.

The splitting of the 124 cm^{-1} E-mode is very clear in our spectra of phase II and this has been noted by Adams and Sharma (1978). The weak Raman mode near 176 cm^{-1} also splits in phase II which was not observed in the previous study. None of the higher frequency modes are affected in the I to II transition. There are several Raman mode crossings and splitting in the region marked phase III and IV. At these points the Raman peaks broaden or narrow as the case may be, and striking changes in their intensity are observed. These are illustrated in figure 4. It is to be noted that there is no discontinuity or change of slope in the pressure dependences of the high frequency Raman peaks (see figure 3), in traversing the sequence of phase transitions from phases I and IV.

The changes in the spectrum across the IV and V phase change are very dramatic.

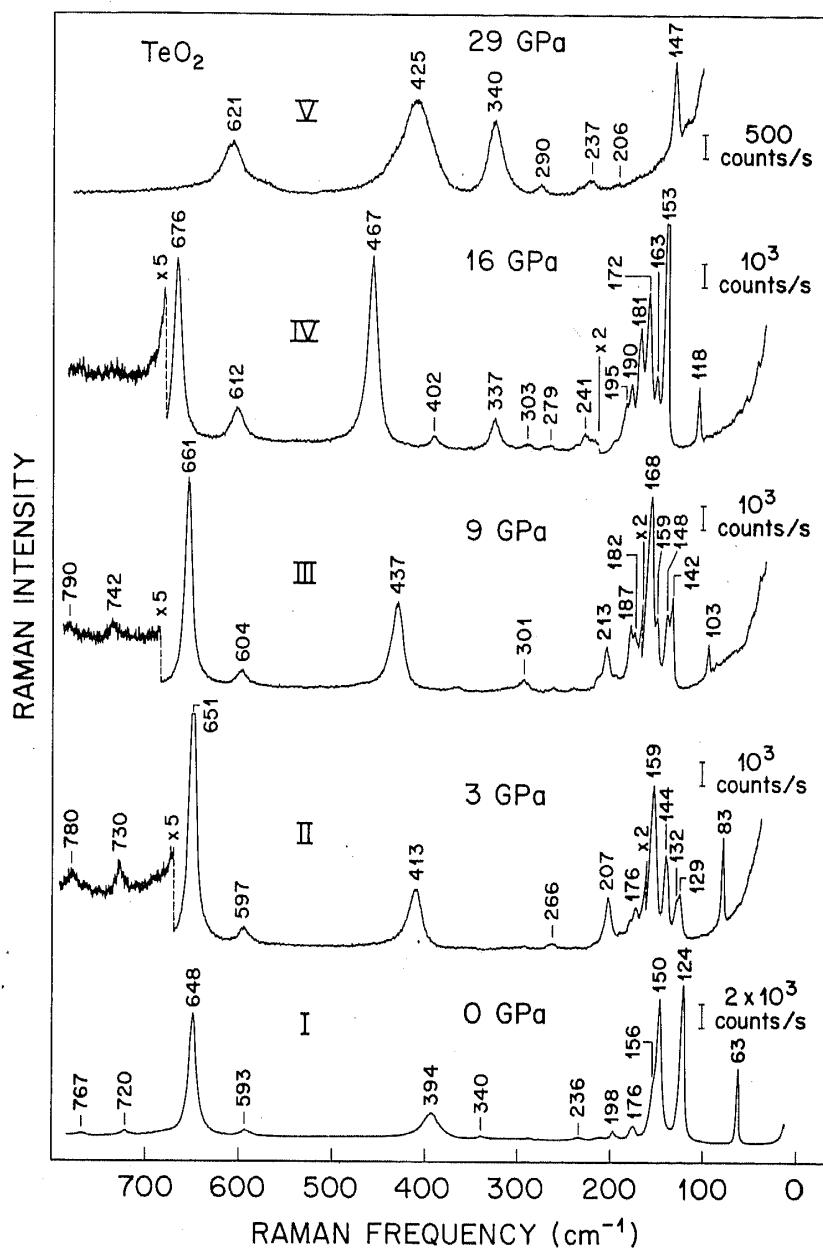


Figure 1. The Raman spectrum of TeO_2 recorded at five different pressures and representative of the five different pressure-induced phases. The spectra of phases I thru IV are quite similar but the spectrum of phase V is totally different. The scale for the Raman intensity is imprinted on the extreme right of each spectrum.

All the Raman peaks shift downward in frequency and broaden strikingly, with the exception of the lowest frequency mode near 147 cm^{-1} (see figure 1 top spectrum marked 29 GPa). The high frequency Raman peaks are the ones that undergo drastic broadening. On release of pressure, the pressure-induced phases revert back to the paratellurite phase, but there is a large hysteresis and mixed phase regions. In fact the $\text{IV} \rightleftharpoons \text{V}$ transition is the most hysteretic of all. On the increasing pressure cycle phase V begins to appear near 22 GPa but complete conversion is seen only in spectra taken near 26 GPa. On releasing pressure cycle phase V persists down to 15 GPa, and thus seems to exhibit the largest hysteresis.

Table 1. Observed Raman peaks of TeO₂ at different pressures.

Phase I 0 GPa cm ⁻¹	Mode* designation	Phase II 3 GPa cm ⁻¹	Phase III 9 GPa cm ⁻¹	Phase IV 16 GPa cm ⁻¹	Phase V 29 GPa cm ⁻¹
63 m	B ₁	83 s 129 m	103 w 142 m	118 m 153 vs	147 s
124 vs	E	132 m 144 m	148 m 159 m	181 m 163 m	206 vw
150 vs	A ₁	159 vs	168 vs	172 s	
156 m	B ₂				
176 w	B ₁ + E	176 w	182 m 187 m	190 m 195 m	237 w
198 w	E(LO)	207 m	213 w	241 w	290 w
236 vw	B ₁ + E	266 vw	301 vw	337 w	340 s
340 vw	E(LO)			402 w	425 s
394 w	A ₁	413 m	437 m	467 s	
593 vw	B ₁	597 w	604 w	612 w	610 w
648 s	A ₁	661 s	661 s	676 s	621 m
720 vw	E(LO)	730 vw	742 vw		
767 vw	E(TO)	780 vw	790 vw		

vs = very strong, s = strong, m = medium, w = weak, vw = very weak.
 *Mode assignment to phase I (paratellurite) peaks.

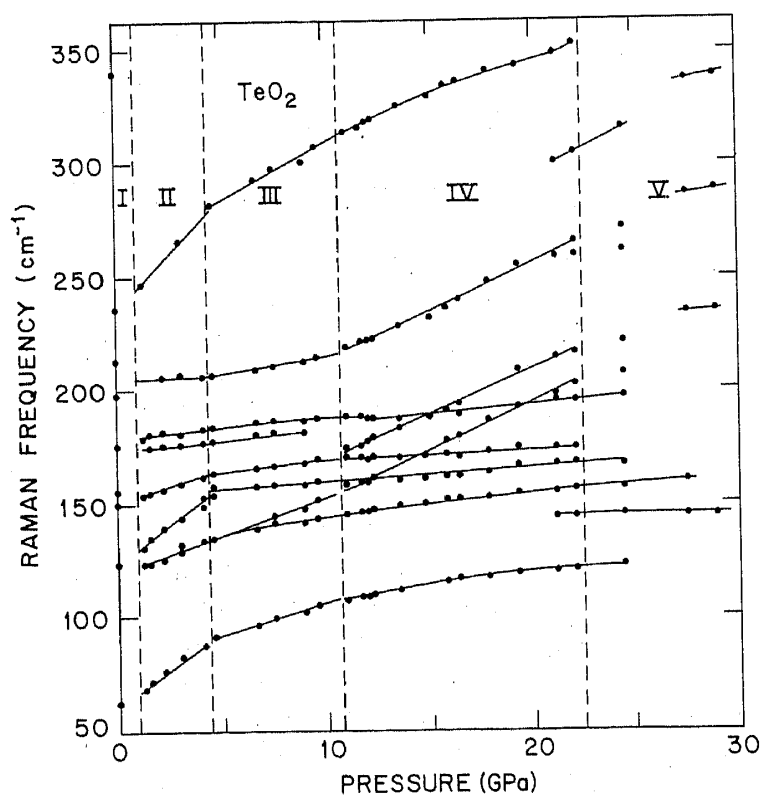


Figure 2. The pressure dependence of the Raman peaks of TeO₂. The dashed lines mark the phase-transition pressures as observed on increasing pressure cycle.

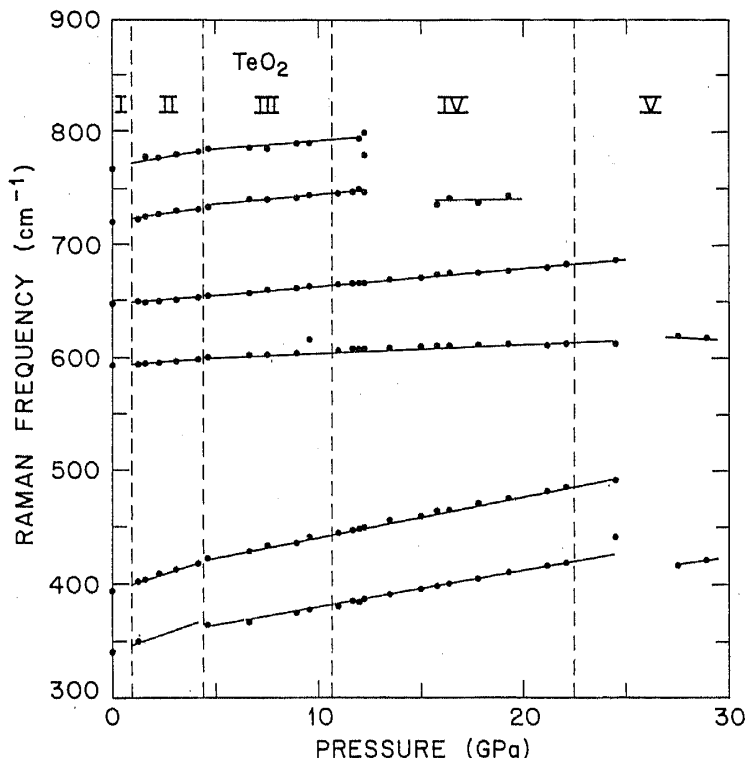


Figure 3. The pressure dependence of the Raman peaks of TeO_2 in the high frequency region. The dashed lines indicate the phase transition pressures from the previous figure.

3. Discussion

Paratellurite (TeO_2) crystallizes in a distorted rutile structure of $D_4^4(P_4, 2_1 2)$ symmetry at atmospheric pressure and the unit cell contains four TeO_2 units (Lindqvist 1968). From symmetry analysis (Pine and Dresselhaus 1972; Ayrault 1972; Durand *et al* 1976) 33 optic modes of $\Gamma_0 = 4A_1 + 4A_2 + 5B_1 + 4B_2 + 8E$ modes are expected of which the A_1 , B_1 , B_2 and E are Raman active, while modes of symmetry A_2 and E are IR active. The mode designation in table 1 are from the published assignments.

The first pressure-induced phase transition near 1 GPa to an orthorhombic structure D_2^4 is well understood and it has been shown that it is a second-order transition purely strain-induced, driven by a soft shear acoustic mode propagating along a $\langle 110 \rangle$ crystal direction and polarized along a $\langle \bar{1}\bar{1}0 \rangle$ crystal direction. Details concerning this transition and its effect on the Raman and IR spectra has already been discussed in the two earlier studies (Percy *et al* 1975; Adams and Sharma 1978). Our Raman results are in general agreement with the findings of Adams and Sharma (1978) in the overlapping region, 0–4.5 GPa. As concluded by the latter authors we also find no evidence for the transition claimed by Kabalkina *et al* 1967 near 3 GPa. However, our Raman data indicate subtle phase transitions near 4.5 GPa and 11 GPa, and a strongly first-order transition near 22 GPa. From the rather remarkable similarity in the Raman spectra of phase II, III and IV, and the absence of any discontinuous changes in the Raman mode frequencies in going from II to III to IV, we conclude that the structural changes at these transitions must be subtle. This would then rule out the CaCl_2 structure for phase III and the PbCl_2 structure for

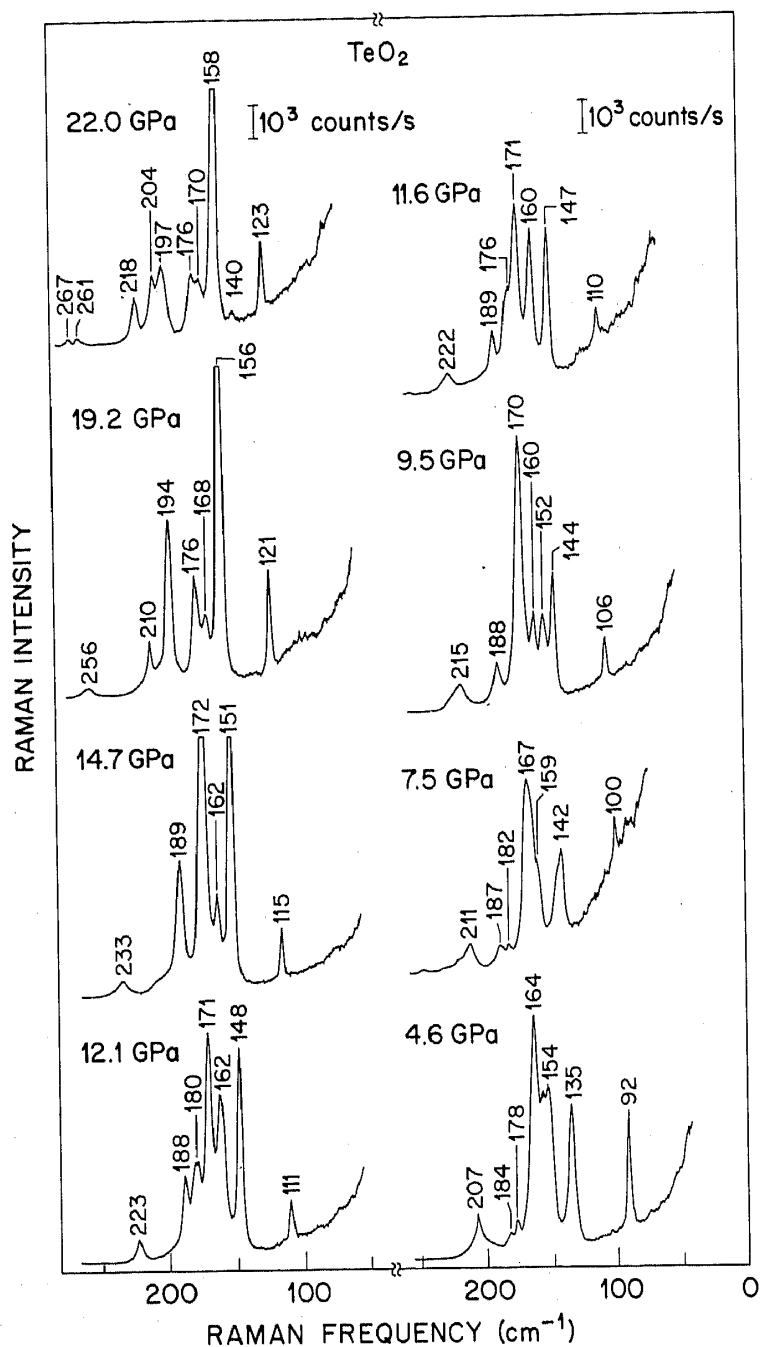


Figure 4. Raman peak structure and their intensities in the low frequency and their intensities at several pressures. The intensities are influenced by pressure-induced mode-crossings and splittings, apart from changes accompanying phase transitions.

phase IV, since transitions to these phases would involve a discontinuous and substantial volume change.

In table 2 we show the mode Grüneisen parameters for phase II calculated from our slope $d\omega_i/dP$ and using the volume compressibility value $k_v = 2.233 \times 10^{-2} \text{ GPa}^{-1}$ of the paratellurite phase. Since phase I to II is a second-order transition we assume that the same value for phase II would be a close approximation. In the last column of table 2 the mode Grüneisen parameters γ_i for phase I obtained by Percy *et al*

Table 2. TeO₂ phase II, mode Grüneisen parameters.

$\omega_i/(\text{cm}^{-1})^*$	$d\omega_i/dP(\text{cm}^{-1}/\text{GPa})$	ω_i^{**}	γ_i^{***}	$\gamma_i(\text{Phase I})^\dagger$
69	6.6	(62)	4.3	1.3
124	3.6	(119)	1.3	1.0
131	6.0	(125)	2.0	—
154	2.7	(151)	0.8	0.5
175	0.7	(174)	0.2	0.8
179	1.0	(179)	0.3	—
209	1.0	(209)	~0.1	0.7
247	0.7	(235)	2.0	0.8
350	4.1	(345)	0.5	0.7
402	5.6	(396)	0.6	0.6
594	1.4	(592)	0.1	0.1
650	1.2	(648)	0.01	0.2
723	2.8	(720)	0.2	0.2
770	3.2	(769)	0.2	0.1

* Phonon frequencies are taken at 1.23 GPa.

** These are ω values obtained from the fitting and referred to $P = 0$.

*** The volume compressibility $k_v = 2.233 \times 10^{-2} \text{ GPa}^{-1}$ of Paratellurite from Percy *et al* (1975) was used to calculate $\gamma_i = 1/k_v(\partial \ln \omega / \partial P)$.

† These γ_i are for phase I set against the corresponding modes of phase II; data from Percy *et al* (1975).

(1975) are given for a comparison. From this it is seen that quite a few modes, in particular the B, mode at 69 cm^{-1} exhibit strikingly large γ_i values. This behavior can also be seen in figure 2.

The basic unit of structure of $\alpha\text{-TeO}_2$ (Lindquist 1968) is built up from four oxygen atoms coordinated to one tellurium atom to form a trigonal bipyramid, with one of the equatorial positions unoccupied. The three dimensional network is built up from TeO_4 units, each oxygen atom being shared by two units, and bonded in the equatorial position to one Te atom and in the axial position to another.

In the Raman spectrum of TeO_2 the high frequency peaks evidently originate from the internal motions of the TeO_4 unit and the low frequency modes are due to the external vibrations, the intermediate frequency region representing vibrational modes of mixed character. The remarkable similarity of the Raman spectra for phases I to IV suggests that the TeO_4 unit remains intact in all these phases, with only minor changes occurring in the linkage of the network. These changes could be the result of small tilting of the unit and consequent change in the symmetry. That the phase transition near 22 GPa must involve a drastic change in the structure is strikingly revealed in the Raman spectrum of phase V. The entire spectral region is affected and all the Raman peaks in phase V broaden, with the exception of the lowest frequency peak. In particular the higher frequency modes which are connected with the internal motions of the TeO_4 unit are broadened and have shifted in their frequencies, strongly suggesting that the structural framework itself has changed.

The $\alpha\text{-TeO}_2$ structure has been described as a distorted rutile structure within a doubled rutile unit cell (Leciejewicz 1961). The high pressure crystal chemistry for a rutile lattice would predict a fluorite or distorted fluorite structure for the high pressure

transition from rutile or distorted rutile structure (Mammone and Sharma 1979; Liu, 1974). However, a transition to a fluorite type lattice would result in a very simple Raman spectrum since only one Raman active mode is predicted for this lattice. For a distorted fluorite structure the symmetry would be lower and a more complex spectrum may be expected. Another possibility would be a direct conversion to a post-fluorite phase (denser than fluorite) such as those found for, ThO_2 , CeO_2 , UO_2 (Liu 1980; Kourouklis *et al* 1988; Block *et al* 1985; Ming and Manghnani 1985). In the case of CeO_2 the high pressure phase transition near 31 GPa has been shown to be from fluorite phase to the PbCl_2 phase (Kourouklis *et al* 1982; Duclos *et al* 1988). In fact a comparison of the Raman spectra of this phase of CeO_2 (Kourouklis *et al* 1988) with that of TeO_2 phase V reveals a striking similarity between the two. Therefore we would like to suggest the PbCl_2 for the high pressure phase V of TeO_2 . A careful high pressure X-ray diffraction study combined with the Raman results can give definitive answers to the structural aspects.

The difficulties in assessing the existence or nonexistence of the high pressure phases in TeO_2 purely from the Raman spectrum are two-fold: the phonon crossings and mode splittings. These complicate the Raman peak structure and the spectra look as if they have changed. However, we have taken this into account in delineating the stability fields and believe in the existence of five phases in the 0 to 30 GPa interval.

4. Summary and Conclusions

Our high pressure Raman studies on TeO_2 (paratellurite) reveals four pressure-induced phase transitions. Of these the transition near 1 GPa is the well studied strain-induced second-order transition arising out of soft acoustic shear mode instability. From the strong similarity of the Raman spectra of phases I to IV we are led to believe that the structure changes involved are subtle in these transitions. However, the IV to V transition represents a major change in structure. It is suggested that this phase transition may be akin to the postfluorite phase of CeO_2 , which has been shown to be the PbCl_2 -type. A high pressure X-ray diffraction study of TeO_2 in the 0 to 30 GPa region would be rewarding, and this study combined with the Raman data should settle the crystal structure of the different phases. Paratellurite (TeO_2) should give a strong X-ray pattern and with a synchrotron source should present no intensity problem.

Optical studies at high pressure would also be possible and argon could be used as a pressure-medium for hydrostatic experiments. The latter would be a distinct advantage since the conventional methanol-ethanol mixture used as a pressure medium in diamond cell work has been found to react with TeO_2 (Adams and Sharma 1978).

Acknowledgement

We would like to acknowledge discussions with Dr G Parthasarathy of Cornell University in connection with the high pressure X-ray diffraction studies of Ming and Manghnani, and that of Liu.

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