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

A JAYARAMAN and G A KOUROUKLIS*

AT&T Bell Laboratories, Murray Hill, New Jersey 07974, USA
*Permanent address: Physics Division, School of Technology, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece

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 $D_{4h}^1$ symmetry to $D_{2d}^1$ 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 $D_{15}^{15}$ symmetry and two tetragonal structures of symmetry $D_{4d}^{15}$ (rutile structure) and $D_{2d}^2$ (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 (Peercy 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 (Peercy 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 $D_4^+$ 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.
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 IV \(\neq\) 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 TeO$_2$ at different pressures.

<table>
<thead>
<tr>
<th>Phase I 0 GPa cm$^{-1}$</th>
<th>Mode* designation</th>
<th>Phase II 3 GPa cm$^{-1}$</th>
<th>Phase III 9 GPa cm$^{-1}$</th>
<th>Phase IV 16 GPa cm$^{-1}$</th>
<th>Phase V 29 GPa cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>63 m B$_1$</td>
<td>129 m</td>
<td>118 m</td>
<td>147 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>124 vs E</td>
<td>132 m</td>
<td>148 m</td>
<td>181 m</td>
<td>206 vw</td>
<td></td>
</tr>
<tr>
<td>150 vs A$_1$</td>
<td>159 vs</td>
<td>172 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>156 m B$_2$</td>
<td>176 w B$_1$ + E</td>
<td>187 m</td>
<td>195 m</td>
<td>237 w</td>
<td></td>
</tr>
<tr>
<td>198 w E(LO)</td>
<td>207 m</td>
<td>213 m</td>
<td>241 w</td>
<td>290 w</td>
<td></td>
</tr>
<tr>
<td>236 vw B$_1$ + E</td>
<td>266 vw</td>
<td>301 vw</td>
<td>337 w</td>
<td>340 s</td>
<td></td>
</tr>
<tr>
<td>340 vw E(LO)</td>
<td>402 w</td>
<td>425 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>394 w A$_1$</td>
<td>413 m</td>
<td>437 m</td>
<td>467 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>593 vw B$_1$</td>
<td>597 w</td>
<td>604 w</td>
<td>612 w</td>
<td>610 w</td>
<td></td>
</tr>
<tr>
<td>648 s A$_1$</td>
<td>661 s</td>
<td>661 s</td>
<td>676 s</td>
<td>621 m</td>
<td></td>
</tr>
<tr>
<td>720 vw E(LO)</td>
<td>730 vw</td>
<td>742 vw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>767 vw E(TO)</td>
<td>780 vw</td>
<td>790 vw</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 TeO$_2$. The dashed lines mark the phase-transition pressures as observed on increasing pressure cycle.
A high pressure Raman study of TeO$_2$

![Raman Frequency vs Pressure Graph]

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 $D^+_2(P_{4}2_{1}2)$ 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 $D^+_2$ 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 $\langle 1\bar{1}0 \rangle$ crystal direction. Details concerning this transition and its effect on the Raman and IR spectra has already been discussed in the two earlier studies (Peercy 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
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 $\gamma_i$ for phase I obtained by Peercy et al.
Table 2. TeO$_2$ phase II, mode Grüneisen parameters.

<table>
<thead>
<tr>
<th>$\omega_0$(cm$^{-1}$)*</th>
<th>$d\omega_0/dP$(cm$^{-1}$/GPa)</th>
<th>$\omega_0$**</th>
<th>$\gamma_1$***</th>
<th>$\gamma_1$(Phase I)$^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>69</td>
<td>6-6</td>
<td>(62)</td>
<td>4-3</td>
<td>1-3</td>
</tr>
<tr>
<td>124</td>
<td>3-6</td>
<td>(119)</td>
<td>1-3</td>
<td>1-0</td>
</tr>
<tr>
<td>131</td>
<td>6-0</td>
<td>(125)</td>
<td>2-0</td>
<td>—</td>
</tr>
<tr>
<td>154</td>
<td>2-7</td>
<td>(151)</td>
<td>0-8</td>
<td>0-5</td>
</tr>
<tr>
<td>175</td>
<td>0-7</td>
<td>(174)</td>
<td>0-2</td>
<td>0-8</td>
</tr>
<tr>
<td>179</td>
<td>1-0</td>
<td>(179)</td>
<td>0-3</td>
<td>—</td>
</tr>
<tr>
<td>209</td>
<td>1-0</td>
<td>(209)</td>
<td>~0-1</td>
<td>0-7</td>
</tr>
<tr>
<td>247</td>
<td>0-7</td>
<td>(235)</td>
<td>2-0</td>
<td>0-8</td>
</tr>
<tr>
<td>350</td>
<td>4-1</td>
<td>(345)</td>
<td>0-5</td>
<td>0-7</td>
</tr>
<tr>
<td>402</td>
<td>5-6</td>
<td>(396)</td>
<td>0-6</td>
<td>0-6</td>
</tr>
<tr>
<td>594</td>
<td>1-4</td>
<td>(592)</td>
<td>0-1</td>
<td>0-1</td>
</tr>
<tr>
<td>650</td>
<td>1-2</td>
<td>(648)</td>
<td>0-01</td>
<td>0-2</td>
</tr>
<tr>
<td>723</td>
<td>2-8</td>
<td>(720)</td>
<td>0-2</td>
<td>0-2</td>
</tr>
<tr>
<td>770</td>
<td>3-2</td>
<td>(769)</td>
<td>0-2</td>
<td>0-1</td>
</tr>
</tbody>
</table>

* Phonon frequencies are taken at 1-23 GPa.
** These are $\omega$ values obtained from the fitting and referred to $P = 0$.
*** The volume compressibility $k_v = 2.233 \times 10^{-2}$ GPa$^{-1}$ of Paratellurite from Peercy et al (1975) was used to calculate $\gamma_1 = 1/k_v(\partial \omega_0/\partial P)$.
$^\dagger$ These $\gamma_1$ are for phase I set against the corresponding modes of phase II; data from Peercy et al (1975).

(1975) are given for a comparison. From this it is seen that quite a few modes, in particular the $B_1$ mode at 69 cm$^{-1}$ exhibits strikingly large $\gamma_1$ values. This behavior can also be seen in figure 2.

The basic unit of structure of $\alpha$-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 $\alpha$-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, ThO₂, CeO₂, UO₂ (Liu 1980; Kourouklis et al 1988; Block et al 1985; Ming and Manghnani 1985). In the case of CeO₂ the high pressure phase transition near 31 GPa has been shown to be from fluorite phase to the PbCl₂ phase (Kourouklis et al 1982; Duclos et al 1988). In fact a comparison of the Raman spectra of this phase of CeO₂ (Kourouklis et al 1988) with that of TeO₂ phase V reveals a striking similarity between the two. Therefore we would like to suggest the PbCl₂ for the high pressure phase V of TeO₂. 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 TeO₂ 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 TeO₂ (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 CeO₂, which has been shown to be the PbCl₂-type. A high pressure X-ray diffraction study of TeO₂ 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 (TeO₂) 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 TeO₂ (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.
References

Ayrault B 1972 Solid State Commun. 11 639
Jayaraman A 1983 Rev. Mod. Phys. 55 65
Leciejewicz J 1961 Z. Kristallogr. 116 345
Liu L G 1980a Earth Planet. Sci. Lett 49 166
Ming L C and Manghnani M H 1982 in High pressure research in geophysics, (eds) S Akimoto and
M H Manghnani p. 329 (Tokyo: Center Academic Publications)
Ming L C and Manghnani M H 1985 in Solid state physics under pressure: recent advances with anvil
devices (ed) S Minomura (Tokyo: KTK Scientific) p. 135