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Phonons in polymorphous PbTe films: II. Infrared and Raman spectra of PbTe and PbTe:Cr films on KCl substrates

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Abstract. The far-infrared (FIR) reflectance of PbTe:Cr films deposited on KCl substrates was investigated. The Raman spectra of samples with prevailing GeS-type phase in the strained sublayer were investigated. More comprehensive information about the optical phonons in PbTe/KCl films was obtained from the parallel investigation of the FIR and Raman spectra. It turned out that frequencies of the Raman-active modes in the GeS-type content of the films are consistent with those measured in bulk PbTe at a hydrostatic pressure of about 6 GPa.

1. Introduction

The presence of high-pressure (HP) orthorhombic GeS- and BCC CsCl-type phases in PbTe films deposited on KCl substrates was proved by x-ray investigations. The HP-phase infrared modes were detected in the far-infrared (FIR) spectra and tentatively assigned. The factor-group symmetry analysis predicts 12 Raman-active modes in a GeS-type phase. Recently Ves *et al* (1989) have reported a Raman study of the GeS-type phase in bulk PbTe under hydrostatic pressure.

Our previous investigations on the process of growth by the laser-assisted deposition (LAD) technique have shown that the doping of the target material increased the speed of growth and thus the relative thickness of the sublayer which is consistent with pressure-induced phases. Moreover, it was shown that for suitable technological conditions the strained sublayer of PbTe:Cr films may be grown mainly in the CsCl-type phase (Baleva *et al* 1985, Baleva and Bakoeva 1986). The purposes of this investigation were

(i) to verify the assignment of the infrared-active phonon modes, studying samples with a prevailing content of one of the HP phases (CsCl or GeS type) and

(ii) to obtain more comprehensive information about the optical phonons in PbTe phases by parallel investigations of Raman scattering and FIR reflectance.

2. Samples and experiments

2.1. Samples

The samples were grown by LAD on KCl substrates. The target materials were PbTe, and PbTe doped with Cr. The technological parameter which was varied was the substrate temperature T_s. It has already been noticed in our early experiments on

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LAD that the CsCl-type phase prevailed in the strained sublayer of the films grown at low substrate temperatures (Baleva 1986). At a substrate temperature higher than about 100 °C the GeS-type phase became dominant.

The x-ray diffractograms, as in the case of PbTe films, indicated the presence of three types of phase (NaCl, CsCl and GeS types) in the PbTe films doped with Cr. The NaCl- and CsCl-type phases were single crystal, with a (100) direction of crystallization, in both doped and undoped samples. The GeS-type phase was polycrystalline in PbTe films, while in PbTe:Cr samples the growth in the (021) direction prevailed. The ratio of the intensities of the CsCl-type phase (100) reflection to the GeS-type phase (200) reflection, which measures the relative content of the HP phases in the strained layers, is much higher in PbTe:Cr films. Moreover, the GeS-type phase can hardly be detected in PbTe:Cr films grown at $T_{\rm s} \simeq 50$ °C (sample N10 in particular). The strained sublayer in these films consists mainly of CsCl-type phase. It was obtained also from the x-ray investigations that the NaCl-type phase in sample N4 is highly misoriented. The latter can be understood if one takes into account that the upper sublayer (with NaCl-type structure) in this sample is relatively thin (about 100 nm).

The data for the samples investigated are summarized in table 1.

Table 1. Sample characteristics and growth temperature $T_{\rm s}$.

Sample No	Thickness		Cr content (at.%)	$T_{\rm s}$ $(\rho_{\rm C})$	Carrier concentration p (10^{17} cm^{-3})
	d(μm)	$d_{\rm FCC}/d_{\rm HP}$			
N10	0.9	0.3/0.6	0.2	50	2.1
N5	0.7	—	0.2	100	3.7
N4	0.5	0.1/0.4	0.2	200	1.7
Cr307C	0.9	—	1.9	200	—
1411	0.1	0.05/0.05	—	200	5.7

2.2. *Far-infrared reflectance*

The FIR spectra of the samples were investigated and interpreted in the way described in part I (Baleva *et al* 1992). The experimental spectra (full circles) of samples N10 and N4 are shown in figure 1 in the range 20–250 cm^{-1}. The parameters for which the best fit between the calculated (full curves) and the experimental (full circles) spectra was obtained are given in table 2. The frequency dependences of the electron damping $\gamma_{\rm p}$ in both samples are shown in figure 2. The electron damping parameters are given in table 3.

2.3. *Raman spectra*

The samples investigated are highly absorbing in the visible range. Moreover, as was pointed out in I, the upper sublayer, with a thickness of over 100 nm, always crystallizes with NaCl-type structure without Raman-active phonons. Thus an extremely low signal had to be detected. The expected phonon frequencies are very close to those of the oxygen rotational Raman lines. To eliminate the air Raman lines the samples were placed in a vacuum chamber.

The room-temperature Raman spectra were excited with the 632.8 nm He–Ne (35 mW power) and 514.5 mn Ar$^+$ (20 mW power) laser lines. The spectra were

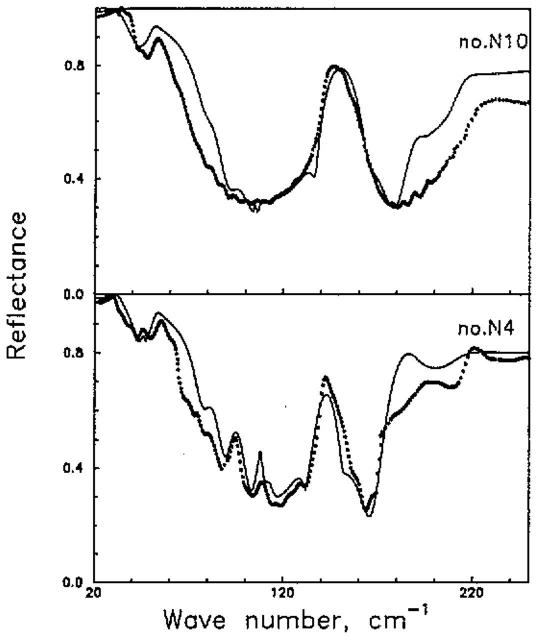

Figure 1. The experimental (●) and calculated (——) reflectance spectra of samples N10 and N4.

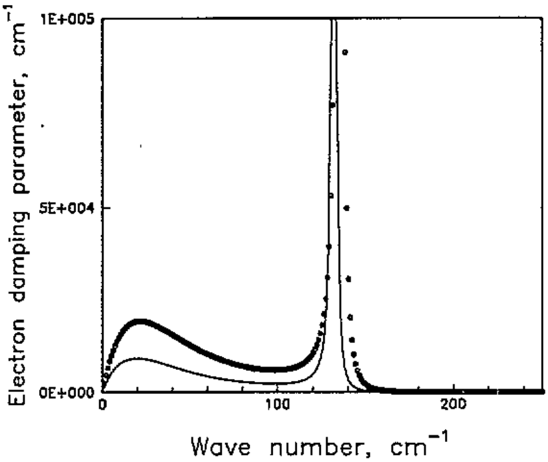

Figure 2. The frequency dependence of the electron damping parameter: ○, sample N10; ——, sample N4.

taken with a Spex 1404 double monochromator in near-back-scattering geometry with a spectral resolution of 3.3 cm^{-1}. Unpolarized Raman spectra of samples 1411 and N4 are shown in figure 3 (the He–Ne plasma lines are denoted by asterisks). As is seen from the figure, clearly resolved Raman peaks appear at 23, 44, 124 and 140 cm^{-1} in the spectrum of sample 1411. All these peaks (with the exception of the peak at 23 cm^{-1}, were also observed in the spectra of the other samples (table 4). A very weak peak was observed at about 105–110 cm^{-1}. Four of these lines with nearly the same peak frequencies have been observed by Ves *et al* (1989) for bulk

Table 2. The parameters of the phonon modes obtained by the fitting procedure in cm^{-1} ($\omega_{t,j}$ and γ_j) and cm^{-2} (s_j).

Material	Sample N10			Sample N4		
	$\omega_{t,j}$	γ_j	s_j	$\omega_{t,j}$	γ_j	s_j
FCC PbTe	32	1	350	32	1	350
BCC PbTe	51	8	105	52	8	102
	—	—	—	46	1	6
Orthorhombic PbTe	82	12	0.8	82	8	1.8
	95	12	0.8	93	8	1.2
	102	12	0.4	107	8	0.6
	118	12	0.2	120	12	0.1
	134	14	0.8	130	12	0.6

Table 3. The electron damping parameters obtained by the fitting procedure.

Electron damping parameter	Sample N10	Sample N4
$b \times 10^5$	15	8
ω_r (cm^{-1})	135	132
ω_0 (cm^{-1})	31	29
ω_p (cm^{-1})	135	120

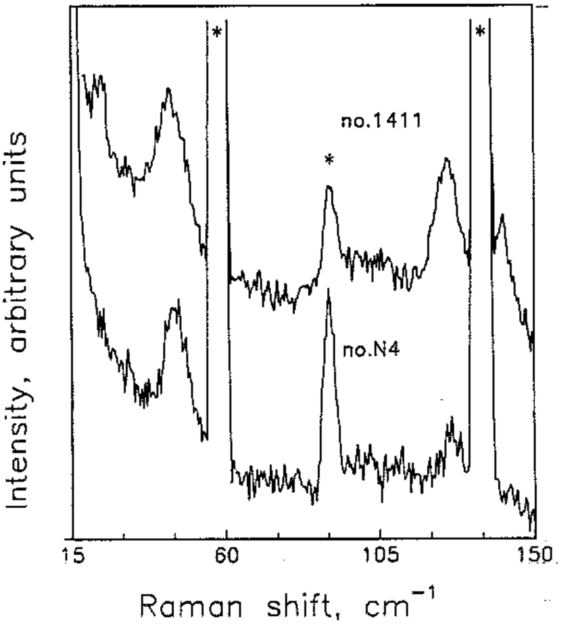

Figure 3. The Raman spectra of samples 1411 and N4, excited by the He–Ne 632.8 nm laser line. The plasma lines are denoted by asterisks.

PbTe under hydrostatic pressure.

Unpolarized Raman spectra of sample N5 were obtained in the Laboratory of the

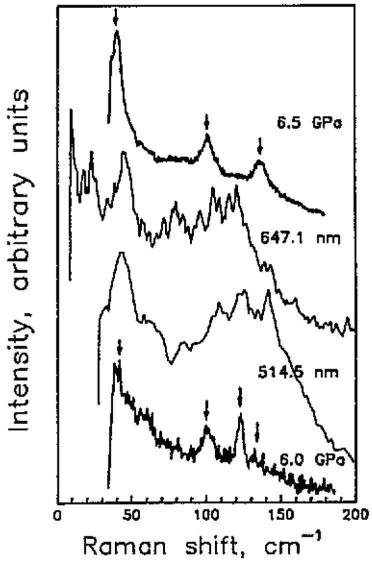

Figure 4. The Raman spectra of the sample N5, compared with the Raman spectra (Ves *et al* 1989) of bulk PbTe under hydrostatic pressure.

Institute of Spectroscopy in Troitck, Russia. Spectra were excited with 514.5 nm Ar$^+$ and 647.1 nm Kr$^+$ laser lines with intensities of about 100 mW in back-scattering geometry. The double-subtractive fore-monochromator (suppression of the laser line background of less than 10^{-11} at 50 cm^{-1}) and the multichannel photoelectric recording system (including an image intensifier, a Vidicon television tube and a computer) enabled low-signal spectra to be obtained (for details see Denissov *et al* (1978, 1987)). In figure 4 the spectra of sample N5 are compared with those obtained by Ves *et al* (1989) at 6 GPa (with (110) planes parallel to the surface) and at 6.5 GPa (with (100) planes parallel to the surface).

3. Discussion

3.1. Infrared-active modes

The most pronounced mode in the FIR spectrum of sample N10 is that at 51 cm^{-1}. The x-ray investigation indicated a prevailing CsCl-type phase in sample N10. Therefore the relation of the TO mode of frequency 50 cm^{-1} (I) to the CsCl-type structure was correct. The comparison of the infrared-active modes in PbTe and PbTe:Cr films (table 2 in I and table 2 in this paper) does not show any significant difference. The Cr content (0.2 at.%) in the films is too low to cause any change in the phonon frequencies.

The phonon damping parameters γ_j and the oscillator strengths s_j were comparable with those of PbTe films (I). This supports the assumption that the main scattering mechanism in this energy range is off dislocations. If the scattering off impurities dominates, the value of the damping parameter in the doped films would be much higher.

3.2. Raman-active modes

First-order Raman scattering by phonons is allowed for the GeS-type structure for which phonons of A_g, B_{1g}, B_{2g} and B_{3g} symmetry are expected to be Raman active.

Table 4. The scaled (ω_s) and the experimental (ω_{exp}) Raman phonon frequencies.

A_g mode								B_{2g} mode							
ω_s	ω_{exp} (cm^{-1})							ω_s	ω_{exp} (cm^{-1})						
	Sample 1411	Sample N4		Sample N5		Sample Cr307C			Sample 1411	Sample N4		Sample N5		Sample Cr307C	
(cm^{-1})	He–Ne	He–Ne	Ar$^+$	Kr$^+$	Ar$^+$	He–Ne	Ar$^+$	(cm^{-1})	He–Ne	He–Ne	Ar$^+$	Kr$^+$	Ar$^+$	He–Ne	Ar$^+$
101	140	143 (weak)	140	145	145	142	142	72	105 (weak)	110 (weak)	—	108	108	—	100(weak)
87	124	125	123	127	127	125	125	—	—	—	—	—	—	—	
48	44	45	43	46	46	46	46	—	—	—	—	—	—	—	
Rigid-layer modes															
22	23	—	—	—	23	—	22	25	—	—	—	—	—	—	—

Ves *et al* (1989) have assigned the Raman peaks in their spectra by scaling the Raman frequencies of GeS according to equation (5) in I (used by us to scale the infrared-active modes). We have obtained the infrared-active modes in orthorhombic PbTe by scaling the infrared-active modes of SnSe; therefore the frequencies of the Raman-active modes were calculated from the SnSe Raman frequencies according to equation (5) in I with $N = 0.75$. The scaled (ω_s) Raman-active A_g and B_{2g} modes experimentally observed in SnSe are given in table 4. The mode assignment for orthorhombic PbTe was made in the setting $D_{2h}^{16} \equiv P_{bnm}$. In table 4 the experimental peak frequencies are related to the corresponding scaled values (at $P = 0$ GPa). The mode with a peak frequency of 23 cm^{-1} was assigned as the A_g mode. This mode cannot be assigned unambiguously as A_g or B_{2g}, as the scaled values ω_s of their frequencies differ by only 3 cm^{-1}. Most probably both modes contribute to the peak at 23 cm^{-1}. On the other hand, it is well known that the intensities of the A_g-symmetry modes are an order of magnitude higher than those of the B_{1g}, B_{2g} and B_{3g} modes. It should be mentioned that the mode at 23 cm^{-1} was not detected in the spectra of all the samples investigated. The latter can be easily understood by taking into account that the value of the pressure coefficient $d\omega/dP$ of this mode is expected to be an order of magnitude higher than that of the other modes (Chandrasekhar *et al* 1977b). In some of the samples this mode obviously appears out of the investigated range ($\omega < 18$–20 cm^{-1}). The frequencies and the assignment of the Raman lines at 44, 124 and 140 cm^{-1} coincide with those obtained by Ves *et al* (1989). The weak peak observed at frequencies from 105 cm^{-1} (sample 1411) to 110 cm^{-1} (sample N4) (at 97 cm^{-1} and 6 GPa in the experiment of Ves *et al* (1989)) was related to the B_{2g} rocksalt-type mode along the a axis. From the comparison of our experimental results with those of bulk PbTe under hydrostatic pressure (Ves *et al* 1989) it can be concluded that the GeS-type phase in the films corresponds to the phase obtained at 6–6.5 GPa hydrostatic pressure. This finding is confirmed by the results of the x-ray investigations. In fact, the unit-cell volume of the GeS-type phase, calculated from the lattice constants (table 1 in I, $V = 235$ Å^3), coincides with that reported by Fujii *et al* (1984) for GeS-type PbTe at a hydrostatic pressure of 6 GPa ($V = 238$ Å^3).

According to Fujii *et al* (1984), two unit cells of NaCl-type structure form the orthorhombic GeS-type unit cell. Then the GeS-type Brillouin zone can be obtained as a result of the folding back of the NaCl-type Brillouin zone. As a result of the folding back of the optical branch, optic modes at the zone centre consist of multiplets (Davydov multiplets). In the GeS-type layer-like structure the Davydov multiplet is considered to be due to the splitting of intralayer modes caused by the interlayer interaction. The magnitude of the frequency splitting of the infrared- and Raman-active doublets provides information about the interlayer interaction. A comparison of Raman- and infrared-active mode frequencies, split according to the predictions of the group theoretical analysis (Chandrasekhar *et al* 1977a), is presented in table 5. The low-frequency A_g and B_{2g} modes, arising from the folding back of the acoustic branch, are rigid shear modes of a layer with respect to its neighbours in the a and c directions. The ratio k/q of intralayer to interlayer force constants is according to Chandrasekhar *et al* (1977a) equal to ω^2/Ω^2, as the frequency Ω of the rigid-layer mode and the frequency ω of the infrared-active mode of the Davydov doublet are proportional to $(2q/M)^{1/2}$ and $(2k/M)^{1/2}$, respectively. As is seen from table 4, in our case the ratio k/q for the intralayer vibration along the a axis only can be deduced from the Davydov splittings: $k/q = (\omega_{B_{3u}})^2_{\max}/(\omega_{A_g})^2_{\min} = 33.9$ for sample N5 and $k/q = 33.5$ for sample 1411. These values are larger than the ratios of the intralayer to interlayer force constants of the orthorhombic A^4B^6 compounds ($k/q = 7$–29), which are regarded as intermediate between layer-like and three-dimensional crystals.

Table 5. Comparison of the experimentally detected Raman- and infrared-active mode frequencies of orthorhombic PbTe.

A_g mode		$E\|a$ B_{3u} mode		B_{2g} mode		$E\|c$ B_{1u} mode	
Sample N5	Sample 1411	Sample N5	Sample 1411	Sample N5	Sample 1411	Sample N5	Sample 1411
145	140	134	136	108	105	93	95
127	124	120	122	—	—	—	—
46	44	45	46	—	—	—	—
23	23	—	—	—	—	—	—

4. Conclusion

We detected five Raman mode frequencies in PbTe and PbTe:Cr films deposited on KCl substrates. The values of the peak frequencies are consistent with those measured by Ves *et al* (1989) in bulk PbTe at a hydrostatic pressure of about 6 GPa, which causes a phase transition from a NaCl-type to a GeS-type structure. Thus it can be concluded that the influence of the mismatch between PbTe and KCl lattice constants (3%) is identical with applying a hydrostatic pressure of about 6 GPa.

The parallel investigation of the infrared- and Raman-active modes made it possible for the ratio of the intralayer to interlayer force constants in PbTe with a GeS-type phase to be evaluated.

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