

Raman spectra of lead chalcogenide single crystals

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Raman spectra of single crystals of lead chalcogenides (PbTe, PbSe, PbS) were studied at room temperature and ambient pressure. The structure of spectra for all compounds is rather similar showing the bands in one- and two-phonon range. Possible spectra identification is discussed.

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1 Introduction

Lead chalcogenide narrow-gap semiconductors PbX (X – Te, Se, S) are applied at sensors of infrared radiation, thermoelectric devices, photoresistors and infrared lasers [1]. These compounds are believed to be close to structural instability [2]. The evidence is high sensitivity of their properties with regard to temperature, doping and pressure. Under high pressures above 2.5–6 GPa and 12–21 GPa lead chalcogenides are known to undergo the electronic and structural phase transitions from NaCl into GeS- and then to CsCl-type of lattices, respectively [1–4]. These materials were studied for many decades, but they still reveal some interesting properties, for example, high temperatures of continuous-wave photoluminescence, which are capable to improve greatly midinfrared lasers [5].

First-order Raman scattering by phonons is forbidden for ambient pressure NaCl structure of lead chalcogenides, so Raman scattering experiments were performed usually on the samples suffered to different structural distortions including mechanical stresses [6], high pressure treatment above phase transition point [7], electrical field [8], chipping of sample into nanocrystalline state [9–11]. Only recently Raman spectra have been observed in NaCl phase of galena (PbS) single crystal [12] under condition of the exciting energy resonance (1.96 eV) with the energy gap $E_1 \approx 1.98$ eV [13, 14]. Authors of [12] interpreted the observed spectra as originated at least partially from forbidden LO(Γ) phonon mode which becomes active due to Fröhlich electron-phonon interaction near resonance. The contribution of the second-order scattering has been also discussed. Analogous Raman spectra for pure rock salt crystals PbSe and PbTe so far were unknown.

Another observation of the Raman spectra in NaCl phase was reported for PbSnSe compounds [15]. The variation of the content and temperature in these compounds leads to the appearance of the gapless state. The measured features in Raman spectra were attributed to electronic excitations because of mentioned inactivity of the first-order phonon scattering and presence of low-frequency electron-hole excitations.

The investigation of the pressure influence on the Raman spectra of PbTe [7] showed that the new lines in spectra appeared prior to the transition to an orthorhombic (GeS) phase. Since lead chalcogenides and its compounds reveal electronic transition to gapless state before structural transition this may be the reason for such behavior. To understand better the features observed in Raman spectra of lead chalcogenides in this work we performed the measurements of pure crystals and its compounds with rock salt

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structure and compared the obtained spectra with theoretical calculations of the phonon dispersion curves. Other aim of this study was to search for evolution of the Raman spectra on the way to gapless state prior to transition to GeS phase which may be shifted to smaller pressures (up to ambient) by chemical substitution of Sn atoms. So, one may expect any anomalies in phonon properties related to gapless state [8] even at ambient pressure.

2 Experiment

For the investigation the single crystals have been taken of p-PbSe, n-Pb_{1-x}Sn_xSe with $x = (0.06, 0.08, 0.125)$, and also of other lead chalcogenides: p-PbS, p-Pb_{1-x}Si_xTe ($x = 0.00005$), p-Pb_{0.786}Sn_{0.314}Te_{0.90} doped with Si (0.001 at. %), and p-Pb_{1-x}Mn_xTe ($x = 0.05$). Raman measurements were performed at room temperatures on freshly cleaved nonoriented samples placed in a vacuum optical chamber. For excitation of Raman spectra 514.5, 488.0 and 476.5 nm lines of argon ion laser were used. Laser beam of up to ~ 40 mW power was focused under 15° angle to the plane of sample's surface into a spot of $\sim 10 \times 40 \mu\text{m}^2$. Scattered light was collected under 90° angle to incident one and was analysed by a double monochromator with single-channel photon counter. Raman spectra were measured from several points of the samples using beam power variation to prevent surface destruction. In most of measurements power density was less than used in [12]. The spectrometer bandwidth was about 3 cm^{-1} .

3 Results and discussion

Room temperature Raman spectra of lead chalcogenides compounds are presented in Fig. 1. The spectrum of single crystal PbS [Fig. 1(a)] measured with 514 nm laser excitation shows three bands at 151, 203 and 443 cm^{-1} . Spectrum intensity for Z(XY)Z polarization geometry is much less than for Z(XX)Z geometry. Such spectra have been already reported in [12]. The difference is small shift in peak energies ($153, 204$ and 454 cm^{-1} in [12]) and the absence of rising baseline at higher frequencies which was discussed as evidence of proximity to E_1 electronic transition. The resonant spectra measured with excitation energy near $E_1 \sim 1.98 \text{ eV}$ were interpreted as enhanced by Frölich electron-phonon interaction. Authors [12] suggested that mode at 204 cm^{-1} is due to forbidden scattering by LO phonon at the center of Brillouin zone and such mechanism contributes also to 2LO scattering at 454 cm^{-1} .

Typical spectra of Pb_{1-x}Sn_xSe single crystals taken with 514 nm excitation are shown in Fig. 1(b). Two broad bands at 135 and 265 cm^{-1} were observed in polarization geometry Z(XX)Z; their intensity is much less in Z(XY)Z geometry. First band shows the structure with features near 130 and 160 cm^{-1} for pure PbSe which shifted to higher energies upon increase of the Sn content ($\sim 5 \text{ cm}^{-1}$ for $x = 0.08$). The spectra intensity increases by $\sim 2-3$ times when spectra were excited with 488 nm (2.54 eV) laser line that indicates resonant effect. Since similar spectra were observed for pure and doped PbSe they cannot be identified as originated from precursors of an orthorhombic phase. By the same reason they cannot be coupled to the electron-hole excitations as it was suggested in [15], where two bands at 85 and 150 cm^{-1} were observed. The energy of first peak at 130 cm^{-1} is close to the frequency of LO mode in the center of Brillouin zone ($\omega_{\text{LO}} \sim 133 \text{ cm}^{-1}$ [16]); second band is observed near double frequency. Thus, one may interpret the obtained spectra as originated from one-phonon and two-phonon scattering by LO vibrations. While the first order Raman scattering is forbidden for NaCl structure the violation of the translation symmetry may activate such scattering by vibrations with $\mathbf{q} \neq 0$. According to neutron data [16] the density of phonon states of PbSe has peaks in the range $60-70 \text{ cm}^{-1}$ coupled to LA and TO vibrations, which are difficult to observe because of strong background and low signal intensity. By the way, TO modes strongly soften with Sn doping [17] while LO modes show only small shifts as it was observed in this work. Possible reason of the observed LO scattering is the resonant Frölich mechanism by forbidden LO phonons [12]. Resonant behavior near $E = 2.54 \text{ eV}$ which is close to the energy of E_2 electronic transition of PbSe near 2.75 eV [13, 14] evidences in favour of such opportunity.

The spectra of third compound of lead chalcogenides family PbTe is seen in Fig. 1(c). The main broad band in low-frequency range of PbTe (doped by Si) spectrum shows the features near 113 and 145 cm^{-1} .

Rather low intensive broad peak was observed at 223 cm^{-1} . All peaks were observed mainly in Z(XX)Z geometry. As in PbS and PbSe the first peak energy is again close to the LO(Γ) frequency ($\omega_{\text{LO}} \sim 114\text{ cm}^{-1}$ [18]) and the high-energy peak has approximately doubled frequency. In Sn-doped PbTe low-energy bands shifted to higher wave numbers by $\sim 2\text{--}3\text{ cm}^{-1}$ and the intensity of band at 223 cm^{-1} becomes negligible. The Te-based compounds often show the presence of Te on the surface or its formation upon the sample destruction with appearance of narrow lines at ~ 125 and 140 cm^{-1} . Since no such lines were found in this study, the observed spectra may be considered as intrinsic for PbTe compounds. The

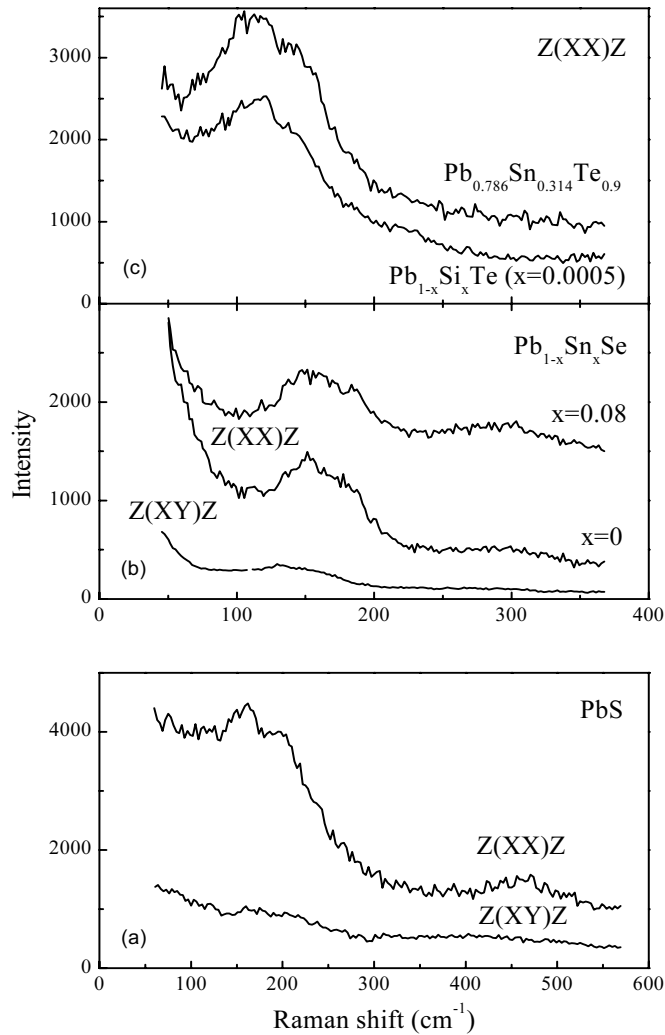


Fig. 1 Raman spectra of lead chalcogenides measured with 514 nm laser line.

critical-point energy E_2 in PbTe is near 2.18 eV. Although there were no indication of resonant behavior in this study, due to closeness of used excitation energy to E_2 and similar spectra structure in all investigated chalcogenides we cannot exclude that low-energy scattering by forbidden LO phonons is enhanced by resonance with electronic transitions and may partially contribute to the observed spectra, as it was proposed in [12].

Finally, one more possibility should be mentioned which explains all spectra as second-order Raman scattering. Thus, according to calculated dispersion curves, density of phonon states and energies of Raman active overtones and combination modes [19] for investigated compounds one could expect the

appearance of “two-phonon” density of states in the range of spectra where Raman bands were found in this study. The observation of found peaks mostly in Z(XX)Z geometry indicates A_{1g} symmetry of the

Table 1 Raman peaks (in cm^{-1}) observed and calculated for lead chalcogenides.

Substance	This work	Theory[19]	Other Raman experiments
PbS	151	153 LA(L)+TA(L)	154 [12]
	203	206 2LA(L)	204 [12] 217 [10, 11]
	443	480 2LO(L)	454 [12]
PbSe	130	122 TO(X)+LA(X)	85 [15]
		124 LO(X)+TA(X)	
	160	124 2TO(Δ)	150 [15]
		140 2TO(X)	
265	140 2LA(Δ),		
	176 2LO(X)		
PbTe	113	266 2LO(Γ)	113 [8]
		103 TO(X)+LA(X)	
	145	124 2TO(Δ)	183 [9]
		156 2LO(X)	
223	230 2LO(Γ)		

spectra to which overtones usually contribute. Table 1 shows the correspondence of measured and calculated spectra. Further studies, in particular, carried out upon change of the temperature and pressure are necessary to refine the origin of the observed spectra in NaCl phase of lead chalcogenides.

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References

- [1] Yu. I. Ravich, B. A. Efimova, and I. A. Smirnov, in: *Methods of semiconductor investigation in application to lead chalcogenides* (Nauka, Moscow 1968).
- [2] O. V. Maksimenko and A. S. Mishchenko, *J. Phys.: Condens. Matter* **9**, 5561 (1997)
- [3] T. Chattopadhyay, H. G. Von Schnering, W. A. Grosshans, and W. A. Holzapfel, *Physica BC* **139–140**, 356 (1986).
- [4] J. Maclean, P. D. Hatton, R. O. Piltz, J. Crain, and R. J. Cernik, *Phys. Res.* **97**, 354 (1995).
- [5] M. Boberl, W. Heiss, T. Schwarzl, K. Wiesauer, and G. Springholz, *Appl. Phys. Lett.* **82**, 4065 (2003).
- [6] M. Baleva, E. Mateeva, *J. Phys.: Condens. Matter* **5**, 7971 (1993).
- [7] S. Ves, Yu. A. Pusep, K. Syassen, and M. Cardona, *Solid State Commun.* **70**, 257 (1989).
- [8] L. Brillson and E. Burstein, *Phys. Rev. Lett.* **27**, 808 (1971).
- [9] A. I. Belogorokhov, L. I. Belogorokhova, D. R. Khokhlov, and S. V. Lemesko, *Semiconductors* **36**, 701 (2002).
- [10] T. D. Krauss, F. W. Wise, and D. B. Tanner, *Phys. Rev. Lett.* **76**, 1376 (1996).
- [11] T. D. Krauss, F. W. Wise, *Phys. Rev. Lett.* **79**, 5102 (1997).
- [12] G. D. Smith, S. Firth, R. J. H. Clark, and M. Cardona, *J. Appl. Phys.* **92**, 4375 (2002).
- [13] S. E. Kohn, P. Y. Yu, Y. Petroff, Y. R. Shen, Y. Tsang, and M. L. Cohen, *Phys. Rev. B* **8**, 1477 (1973).
- [14] E. A. Albanesi, C. M. I. Okoye, C. O. Rodriguez, E. L. Peltzer y Blanca, and A. G. Petukhov, *Phys. Rev. B* **61**, 16589 (2000).
- [15] L. K. Vodop'yanov, L. A. Falkovskii, J. Irvin, and S. Himenis, *JETP Lett.* **53**, 561 (1991).
- [16] L. K. Vodop'yanov, I. V. Kucherenko, A. P. Shotov, and R. Sherm, *JETP Lett.* **21**, 101 (1978).
- [17] P. R. Vijayraghavan, S. K. Sinha, and P. K. Iyengar, *Proc. Nucl. Phys. Solid State Phys. (India)* **16C**, 218 (1973).
- [18] W. Cohran, R. A. Cowley, G. Dolling, and M. M. Elcombe, *Proc. Roy. Soc.* **A293**, 433 (1966).
- [19] K. S. Upadhyaya, M. Yadav, G. K. Upadhyaya, *Phys. Stat. Sol. (b)* **229**, 1129 (2002).