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A Raman study of high-pressure phases of lead chalcogenides PbX (X = S, Se, Te)

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Pressure-induced phase transitions of lead chalcogenides were studied by Raman spectroscopy. The number of Raman modes observed for the first high-pressure phases was found to be significantly less than expected from selection rules for the proposed GeS-type orthorhombic structure. The observations are consistent with the alternative assignment as CrB-type. In the case of PbS, the disappearance of the intermediate-phase Raman lines in the pressure range of 19–25 GPa, i.e., in the vicinity of the orthorhombic to CsCl-type phase transition, is accompanied by a strong increase in a structureless background. The Raman background is attributed to light scattering by charge carriers in the metallic CsCl-type phase.

Keywords: Raman scattering; lead chalcogenides; pressure; phonons; semiconductor to metal transition

1. Introduction

The lead chalcogenides PbX (X = S, Se, Te) represent prototype narrow-gap semiconductors. They find application in Peltier cooling, infrared radiation detection, diode lasers, and thermophotovoltaic energy converters. At ambient conditions, the PbX crystallize in the rocksalt-type structure (B1, space group Fm-3m). Early high-pressure investigations by X-ray diffraction and electrical transport methods have shown the PbX to undergo a number of phase transitions, see, e.g., [1–11]. At pressures of 2.5–6 GPa, the PbX transform to ‘intermediate’ orthorhombic phases. Three different structure types, i.e., GeS (B16, Pnma), FeB (B27, Pnma) and CrB/TI (B33, Cmcm), have been proposed for the intermediate phases [3,10–13]. At pressures of 13–25 GPa, the PbX adopt the eightfold-coordinated CsCl-type structure (B2, Pm-3m). A detailed discussion of transition pathways from the B1 to the B2 structures via intermediate orthorhombic phases is presented in [14]. The B2 phases are reported to be metallic and superconducting [1,5,6,9,15]. The effect of pressure on the electronic structure of the PbX has been addressed in several theoretical studies, e.g., [16–18].
Concerning inelastic light scattering, no first-order Raman scattering by phonons is expected for the B1 phases. However, Raman features of a different origin have been observed in all B1-type PbX [19–22]. First-order Raman scattering is allowed for the proposed orthorhombic phases. It appears that so far only the phase behavior of PbTe has been studied by high-pressure Raman spectroscopy [23].

Here we report selected results of high-pressure Raman measurements of the binary PbX and the alloy compound Pb$_{0.875}$Sn$_{0.125}$Se. The main interest is in detecting the pressure-induced structural modifications optically, in elucidating the relation between structure and phonons in the orthorhombic phases, and in following changes in Raman scattering at the semiconductor to metal transitions.

2. Experiment

The experiments were performed using single-crystal platelets with dimensions 50 × 50 × 10 μm. They were loaded into a gasketed diamond anvil cell (DAC) using a 4:1 methanol–ethanol mixture as a pressure medium. Pressure was measured by the ruby luminescence method. The Raman spectra were excited by low-power laser radiation (nominally 1 mW outside the DAC) at wavelengths of 514 and 633 nm, and they were recorded by Renishaw and Labram microscope spectrometers, providing a focal spot on the samples of 2–10 μm diameter, depending on settings. The spectral resolution was about 3 cm$^{-1}$. The measurements were performed for pressures up to 10–12 GPa for the selenide and telluride compounds. In the case of PbS, they were extended up to 40 GPa.

3. Results and discussion

Figure 1(a) shows representative Raman spectra (514 nm excitation) of the B1 and orthorhombic phases of all investigated samples. Close to the ambient pressure, we find broadbands located near 120 and 140 cm$^{-1}$ (PbTe), 130–135 cm$^{-1}$ (PbSe and PbSnSe) and 155 and 200 cm$^{-1}$ (PbS). Such features were observed previously [19–22], and in the case of PbS, their interpretation has been the subject of recent temperature-dependent Raman studies of natural and isotopically substituted samples [19,21,22]. Our measurements on samples from different batches show that the intensity of these broadbands varies. So, their origin may in part be related to nonstoichiometry. Raman bands in the high-frequency two-phonon region could also be observed in PbS (450 cm$^{-1}$) and PbSe (260 cm$^{-1}$). The origin of the relatively strong two-phonon intensity is discussed in [19,21,22].

The transitions to the orthorhombic phases are accompanied by the appearance of narrow strong lines near 120 cm$^{-1}$ (PbTe), 155 cm$^{-1}$ (PbSe and PbSnSe) and 225 cm$^{-1}$ (PbS). Other relatively strong lines appear near 65 cm$^{-1}$ in PbSe and 75 cm$^{-1}$ in PbS; note that their recorded intensities are affected by the cutoff of notch filters. Careful microscopic observations revealed that the surfaces of all samples developed a domain-like pattern at the B1 to orthorhombic transition. In the case of PbS, polarized Raman measurements were carried out on different domains of unknown orientation. The polarization dependence of the two intense Raman modes mentioned above implies A$_{1g}$ symmetry. A third line seen for PbS near 120 cm$^{-1}$ has a different symmetry; it cannot be identified without knowledge of the orientation of a given domain. Our observations suggest that single-crystal-like regions exist in the orthorhombic phase. Their formation can explain why the number of observed Raman lines varied with the focal spot position on the sample surface. Figure 1(b) demonstrates this effect for PbS at 3.5 GPa.
Figure 1. (a) Raman spectra of lead chalcogenides measured at two pressures using 514 nm excitation. Arrows point to the positions of Raman features of the initial B1 and intermediate orthorhombic phases. Numbers refer to pressure in gigapascal. (b) Raman spectra of PbS (633 nm excitation) in the cubic B1 phase and after the transition to the orthorhombic phase (3.5 GPa). The two upper spectra were taken at the same pressure, but from different points of the sample.

In the orthorhombic phases, several low-intensity peaks were observed, i.e., near 125 and 180 cm$^{-1}$ in the ternary compound PbSnSe, near 100 and 137 cm$^{-1}$ in PbTe and at 160, 200 and 270 cm$^{-1}$ in PbS. The pressure dependences for all reproducible lines of the PbS and PbSe compounds are shown in Figure 2(a) and (b). For all compounds, the B1 to orthorhombic transition pressures derived from the Raman experiments coincide well with results obtained by X-ray diffraction and electrical transport methods. Due to hysteresis, the Raman lines of the orthorhombic phases were observed at lower pressures upon unloading compared with increasing pressure (Figure 2(b)). We do not show here our pressure dependences of phonon Raman lines for PbTe because they were found to be essentially the same as those reported in [23]. In that earlier work, the spectra were taken with 647 nm excitation and one more peak near 40 cm$^{-1}$ was observed.

The pressure coefficients for the most intense Raman lines of the orthorhombic phases are 2.17(5) cm$^{-1}$ GPa$^{-1}$ for PbTe (120 cm$^{-1}$ mode), 3.68(4) cm$^{-1}$ GPa$^{-1}$ for PbSe and PbSnSe (155 cm$^{-1}$ mode) and 3.42(6) cm$^{-1}$ GPa$^{-1}$ for PbS (225 cm$^{-1}$ mode). For PbS, the corresponding estimated mode Grüneisen parameter is 0.49(7) (assuming a bulk modulus $B_0 = 30.1$ GPa [12]).

Different Raman selection rules apply to the proposed orthorhombic structure types. The GeS-type structure has 12 Raman-active phonons ($4A_{1g} + 2B_{1g} + 3B_{2g} + 2B_{3g}$). All Raman-allowed phonons were observed for GeS and GeSe [24,25] and eight to nine of them were clearly seen in experiments on SnSe and SnS single crystals [26]. For the CrB- or TlI-type structure, only six modes are Raman-active ($2A_{1g} + 2B_{1g} + 2B_{3g}$). So, the observation of only two strong lines with the (possible) $A_{1g}$ symmetry in the binary compounds PbS and PbSe and the small total number of observed lines seems to favor the $Cmcm$ symmetry. This would be consistent with the structure-type assignments discussed in [10–12]. Of course, attributing $Cmcm$ symmetry on the basis of Raman spectra cannot be conclusive at this point. For instance, there may be Raman modes with energies 60 cm$^{-1}$, which could not be observed with our technique. A more firm conclusion would be possible if our Raman data were compared to phonon frequencies calculated for both possible structure types.
We note that for the ternary compound PbSnSe, a high-frequency mode at 180 cm$^{-1}$ appears in the intermediate phase (not shown in Figure 2(b)). The back-extrapolated ambient-pressure frequency of this mode is 169 cm$^{-1}$. The highest Raman phonon frequency of A$_{1g}$ symmetry in orthorhombic SnSe was observed at 151 cm$^{-1}$ [26]. Thus, the appearance of the high-frequency mode may indicate a two-mode behavior in this mixed crystal or the activation of Raman-forbidden vibrations.

One more notable feature was observed in the Raman spectra of PbS (Figure 1(b)). As mentioned, a doublet-like two-phonon structure near 450 cm$^{-1}$ was earlier observed at ambient conditions [19–22]. When increasing the pressure to 2.1 GPa in the initial rocksalt phase, the two-phonon feature hardly shifts. At the structural transition, the intensity maximum of the two-phonon scattering jumps in frequency to 490 cm$^{-1}$ (at 3.5 GPa, see Figure 1(b). The origin of the two-phonon feature in the B1 phase was attributed to overtone LO phonon scattering enhanced by the Fröhlich interaction under resonance conditions [19,21,22]. A similar mechanism may be responsible for the relatively large intensity of the two-phonon feature in the orthorhombic phase. Its ‘hardening’ by about 10% relative to B1 can in part be attributed to the 4.7% decrease in the molar volume [12]. A LO phonon–plasmon interaction may possible contribute to the large frequency jump. This is because at the phase transition the charge carrier concentration in the surface layer of single-crystal-like domains may increase. Further studies are needed to clarify this point.

Our measurements on PbS were extended up to 40 GPa. This range covers the second transition from the intermediate orthorhombic to the CsCl-type phase. The transition occurs near 21.5 GPa according to [10], but the authors of [11] noted that traces of the orthorhombic phase were still observed at much higher pressures. We found that at selected sample spots the characteristic Raman lines of the intermediate phase persisted for pressures up to 40 GPa (Figure 2(a)).

Investigations of PbS by electric transport methods showed that PbS becomes ‘metallic’ already at 12 GPa (thermopower measurements [15]) or at 18 GPa (resistance measurements [6]). Both pressure values are less than the ones reported for the transition to the CsCl (B2) phase. Hence,
the metallic nature seen in the stability range of the orthorhombic phase presumably arises from a high concentration of defects.

As for the B2 phase of PbS, it was shown to be superconducting, with a transition temperature of 6.3 K [9]. The results of band structure calculations for B2-PbS at an unidentified lattice constant [17, Figure 5] are consistent with a metallic state. As a quick check, we have carried out band structure calculations of PbS using the LMTO method in the LDA approximation. The spin-orbit coupling was not included. While B1-PbS at the ambient-pressure lattice parameter was found to be a semiconductor with a gap of about 0.3 eV, B2-PbS was found to be metallic for a lattice parameter of 3.289 Å which is close to experimental values reported for the B2 phase. The ‘negative gap’ of B2-PbS was found to be of the order 1.5 eV.

Raman-allowed first-order phonon scattering is not expected in the B2 phase. Figure 3 shows that phonon Raman lines of PbS disappear between 19 and 25 GPa, i.e., during the sluggish transition toward the B2 phase. At the same time, a strong and reversible increase in a structureless background was observed in this pressure range. We attribute it to light scattering by free charge carriers. The phenomenon can possibly be used for a more detailed low-temperature investigation of the metallic state of lead chalcogenides.

In summary, pressure-induced structural and semiconductor metal transitions in PbSe and PbS compounds have been investigated by Raman scattering. It was shown that phonon as well as electronic light scattering may serve as a useful tool for the investigation of structural and electronic properties in lead chalcogenides under pressure.

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