Raman spectra of \((\text{PbS})_{1.18}(\text{TiS}_2)_2\) misfit compound

Sergey V. Ovsyannikov\textsuperscript{a,b,∗}, Vladimir V. Shchennikov\textsuperscript{a}, Andres Cantarero\textsuperscript{b}, Ana Cros\textsuperscript{b}, Alexander N. Titov\textsuperscript{a}

\textsuperscript{a} Institute of Metal Physics of Russian Academy of Sciences, Urals Division, GSP-170, 18 S. Kovalevskaya Str., Yekaterinburg 620041, Russia
\textsuperscript{b} Institut de Ciencia de Materials, Universitat de Valencia, P.O. Box 22085, E46071 Valencia, Spain

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Abstract

A Raman study on the \((\text{PbS})_{1.18}(\text{TiS}_2)_2\) semiconductor structure with incommensurate layers (misfit) is reported. The different bands observed in the spectra are attributed to both the \(\text{TiS}_2\) host layers, at 219 (\(\text{E}_g\)) and 333 (\(\text{A}_{1g}\)) \text{cm}^{-1}, and the intercalated \(\text{PbS}\) layers: the \(\text{LO} (\Gamma_1)\), \(2\text{LO}\) and \(3\text{LO}\) phonons at 203, 412 and 634 \text{cm}^{-1}, respectively. A phonon peak probably related to the superposition of \(\text{TiS}_2\) and \(\text{PbS}\) vibrations, was observed near 286 \text{cm}^{-1}. The decrease of the phonon wave numbers (of the modes located at 203, 333, 412, and 634 cm\(^{-1}\)) with increasing laser power pointed out negative temperature coefficients of these modes. A peak appearing with laser power near 151 cm\(^{-1}\) is discussed. For higher laser powers the formation of oxides and oxysulfates complexes (\(\text{PbO}, \text{TiO}_2, \text{PbO}_2, \text{PbSO}_4, \text{"PbO-PbSO}_4"\)) at the misfit’s surface was observed from the Raman spectra. In the low-frequency region the peaks at 19, 73 and 95–96 cm\(^{-1}\) have been revealed associated presumably with vibrations of the \(\text{PbS}\) layers.

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1. Introduction

Layer dichalcogenides of Ti and their intercalates are perspective materials for applications due to their highly anisotropic and unusual electrical and mechanical properties [1–6]. The layer misfit crystal \((\text{PbS})_{1.18}(\text{TiS}_2)_2\) consisting of alternate layers of \(\text{PbS}\) and \((\text{TiS}_2–\text{TiS}_2)\) may be considered as a product of the intercalation of \(\text{PbS}\) into a \(\text{TiS}_2\) matrix. Fig. 1 shows a projection of the crystal structure in the \(bc\) plane, \(c\) being the direction perpendicular to the layers. The layers are bonded by weak van der Waals interaction [1,2]. In the plane of the layers, the \(\text{PbS}\) lattice is distorted in comparison to the bulk compound with NaCl structure (the cubic unit cell parameter of \(\text{PbS}\) is \(a = 5.936\ \text{Å}\)), while the \(\text{TiS}_2\) structure is almost identical to that of the bulk material. In the \(b\)-direction, the \(\text{PbS}\) and \(\text{TiS}_2\) fragments have the same unit cell parameter \((b = 5.936\ \text{Å})\), whereas in the \(a\)-direction they are incommensurate (misfit): \(a = 5.761\ \text{Å}\) for \(\text{PbS}\) and \(3.390\ \text{Å}\) for the \(\text{TiS}_2\) layers. Thus, the ratio of \(a(\text{TiS}_2)\) over \(a(\text{PbS})\) is irrational and approximately equals 0.5884395…, resulting in the chemical formula \((\text{PbS})_{1.18}(\text{TiS}_2)_2\).

Raman spectra of complex systems can manifest the phonons of both subsystem and their superposition [7]. Misfit layer compounds were found to exhibit shifts in polar phonon frequencies of host layers supposedly due to a charge transfer between host matrix and guest layers [8]. Vibrational structure of guest layers in misfits differs from that of bulk samples [7] as they have a different bonding between atoms. Bulk \(\text{PbS}\) single crystals possess a NaCl structure at ambient conditions and the first-order Raman scattering is forbidden. \(\text{PbS}\) layers in misfit possess a lower symmetry than NaCl lattice since they are distorted along the \(a\)-axis in the plane and, hence, one may expect the appearance of the first-order spectra.

In similar misfit—\((\text{PbS})_{1.18}\text{TiS}_2\) (without van der Waals gaps) Sourisseau et al. experimentally observed four phonon peculiarities at 203, 292, 336, and 416 cm\(^{-1}\) [9–12]. But Hangyo et al. reported the modes at \(\sim 40, \sim 80, 190, 225,\) and 329 cm\(^{-1}\) [7]; the first three phonons were assigned to \(\text{PbS}\) [7], whereas the last two ones – to \(\text{TiS}_2\) layers [7]. Recently Smith et al. [13] and Sherwin et al. [14] had a success in separation of “own” and “oxide” phonons in single crystal of galena (\(\text{PbS}\)) and established the first- and second-order Raman spectra. So, presently a novel study on similar misfits is required in order to settle the
Fig. 1. Projection of the layer misfit (PbS)\(_{1.18}(\text{TiS}_2)_2\) structure along [1 0 0]. The dashed rectangle shows the primitive cell. The solid lines are bonds inside of the layers (PbS, TiS\(_2\)), while the dashed lines are bonds between the layers. The rhombuses point the location of octahedral voids. The closed symbols correspond to atoms in the plane of the figure, whereas the open ones to atoms in the plane below that.

existing discrepancies and to give a correct interpretation of the spectra.

So, the goal of this work was twofold: (i) to investigate the "own" vibration of PbS layers in the misfit and (ii) to study the influence of PbS intercalation on the phonon frequencies of TiS\(_2\) and the possible appearance of superposition vibrations. In order to distinguish the "own" and surface-oxydization-induced spectra we performed a comparative study under variation of laser power in a wide range.

2. Experiment

The misfit (PbS)\(_{1.18}(\text{TiS}_2)_2\) compound was grown by "gas-transport reaction" techniques using PbS and TiS\(_2\) powders in the corresponding amounts \(\sim 0.59\) and \(1.00\). The X-ray powder pattern as well as lattice parameters were the same as in Ref. [2].

The Raman spectra were excited by an Ar-ion laser (488.0, 514.5 nm lines) at several laser powers and were analysed by a Jobin Yvon T64000 confocal micro-Raman spectrometer equipped with dispersive gratings of 1800 gr/mm. The experiments were performed either in double subtractive mode or using the spectrograph with a Notch filter (514.5 nm excitation). All spectra were collected in backscattering geometry along the Z-direction with a spectral resolution of \(\sim 0.5\) cm\(^{-1}\) and detected with a nitrogen cooled charge-coupled device detector. For the spectra investigated at ambient conditions (10–750 cm\(^{-1}\) range) a microscope objective with a magnification of 100 was used to excite and collect the signal. In these conditions, the diameter of the laser spot on the sample surface is around 1 \(\mu\)m. The experiments were performed in parallel (XX) and crossed (XY) polarisation geometries. The samples were films with the typical sizes \(\sim 10 \mu\text{m} \times 100 \mu\text{m} \times 100 \mu\text{m}\). Under increase of the laser power the spectra were gathered each time from the different novel points at the misfit surface, while under decrease of one—in the same point. The real laser power (given in the figure captions) at the sample surface was measured locating a power-meter in the place of the sample.

Low-frequency Raman spectra were studied separately in a micro-cryostat (Cryovac). For these experiments a microscope objective with a magnifying power of 50 and large working distance was used as focusing lens. Both bulk and thin solid film pieces of PbS single crystals were measured for comparison at the same experimental conditions.

3. Experimental results and discussion

Table 1

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Possible origin</th>
<th>Data of other works</th>
</tr>
</thead>
<tbody>
<tr>
<td>19 ± 1</td>
<td>PbS, LA(X) – TA(X)</td>
<td>80 ± 2(^b) [7], 68(^b) [19–21]</td>
</tr>
<tr>
<td>73</td>
<td>PbS, 2TA phonon</td>
<td>93–95(^c) [24]</td>
</tr>
<tr>
<td>95–96</td>
<td>PbS, LA(X) + TA(X)</td>
<td>154(^d) [13]</td>
</tr>
<tr>
<td>151</td>
<td>PbS, TA + TO</td>
<td>203(^a,10), 204(^b) [13]</td>
</tr>
<tr>
<td>203</td>
<td>PbS, LO((\Gamma))</td>
<td>225(^b) [7], 227(^b) [15]</td>
</tr>
<tr>
<td>219</td>
<td>TiS(_2), E(_g) mode</td>
<td>229(^a) [9]</td>
</tr>
<tr>
<td>286.5</td>
<td>superposition mode</td>
<td>329(^b) [7], 336(^b) [9]</td>
</tr>
<tr>
<td>333</td>
<td>TiS(<em>2), A(</em>{1g}) mode</td>
<td>335(^b) [15]</td>
</tr>
<tr>
<td>412</td>
<td>PbS, 2LO</td>
<td>415(^b) [20], 416(^a) [9]</td>
</tr>
<tr>
<td>632</td>
<td>PbS, 3LO</td>
<td>454(^a) [13]</td>
</tr>
</tbody>
</table>

\(^a\) Observed in “similar” misfits.  
\(^b\) In PbS nanocrystal.  
\(^c\) In PbS single crystal.  
\(^d\) In TiS\(_2\) single crystal.
Fig. 2. Raman spectra of the layer misfit single crystal (PbS)_{1.18}(TiS_2)_2 at T = 298 K excited by the 514.5 nm laser line. Every spectrum corresponds to the average of several spectra collected during 500 s periods each. Curve 1 corresponds to parallel (XX) polarisation while curves 2–5 were obtained with crossed (XY) polarisations: 1—"own" spectrum collected at ∼4 mW averaging 8 spectra (4000 s in total); 2—"own" spectrum collected at ∼2.5 mW by averaging 12 spectra; the spectrum exhibits a new phonon at 151 cm\(^{-1}\); 3—"transient" spectrum obtained with a laser power of ∼6.5 mW averaging 12 spectra; the spectrum exhibits a new phonon at 151 cm\(^{-1}\); 4 and 5—"oxidized" spectra corresponding to twofold collection with ∼7.5 and 8 mW, respectively. The arrows indicate the "own" peaks of the misfit.

by Hangyo et al. on "PbTiS_3" misfit [7], while no shift was registered by Sourisseau et al. [9–12] on (PbS)\(_{1.18}\)TiS\(_2\). The remaining allowed bands of TiS\(_2\) (227 and 380 cm\(^{-1}\) in TiS\(_2\) single crystals [15] were hardly seen in the spectra. Only in a couple of spectra obtained under XY polarisation we did observe some "hidden" phonon peak in the misfit near 219 ± 2 cm\(^{-1}\) (Fig. 2, curve 2), which may be associated with the E\(_{g}\) mode of TiS\(_2\) at 227 cm\(^{-1}\) [7]. The TiS\(_2\) phonon at 380 cm\(^{-1}\) is a right shoulder of the A\(_{1g}\) mode (335 cm\(^{-1}\)) even in the spectra of TiS\(_2\) single crystals [15,7]. Probably this phonon mode also soften under PbS intercalation and is fully covered by the wide 333 cm\(^{-1}\) phonon; the asymmetric shape of the 333 cm\(^{-1}\) mode pointed in that direction (Fig. 2, curves 1 and 2). The broad peculiarity with a maximum near ∼510 cm\(^{-1}\) appearing with the increase of laser power might be due to formation of PbO\(_2\) [17] or TiO\(_2\) [18] films at the misfit surface.

We may conclude that the A\(_{1g}\) mode of TiS\(_2\) (out-of-plane vibrations) was tolerant to the intercalation (a shift from 335 to 333 cm\(^{-1}\)) as it was predicted by the general theory for misfits [8]. However, the behaviour of the E\(_{g}\) mode (in-plane vibration)—a softening from 227 to 219 cm\(^{-1}\) (∼3.5%) distinguished from the typical behaviour of some other Ti-free misfit compounds (increase in wave number by 10–20% [8]). This circumstance attested about the unusual phonon properties of Ti-based misfits and may be explained by structural peculiarities: in TiX\(_2\)-based misfits (X = Te, Se, S) the Ti atom has an octahedral instead of prismatic coordination [8].

The peculiarities observed at 203, 412, 632 cm\(^{-1}\) may be assigned to the LO phonon (Raman forbidden in the NaCl lattice) of the PbS layer and its first (2LO) and second (3LO) overtones. Similar Raman frequencies were established earlier in PbS nanocrystals [19–22]. Another phonon peak at 154 cm\(^{-1}\) revealed in PbS single crystals by Smith et al. [13] and identified as a combination of TA and TO phonons was observed at 151 cm\(^{-1}\) in the present work under the essential enhancing of laser power (Fig. 2, curve 3). Earlier, in a study on similar misfits only the LO phonon was distinctly observed at 194 and 189 cm\(^{-1}\) and was associated with PbS layers [7].

The peak at 286.5 cm\(^{-1}\) is probably a superposition of phonon modes of TiS\(_2\) and PbS layers [9]. A similar phonon peculiarity at 292 cm\(^{-1}\) was observed in Refs. [9,10].

The dependencies of the 203, 333, 412 and 632 cm\(^{-1}\) phonon bands wave numbers on the laser power in the misfit correspond to negative temperature coefficients of these modes (Fig. 3), likely due to thermal extension and a weakening of the chemical bonds in the lattice. These results agree well with the data obtained for the 335 cm\(^{-1}\) phonon peak in TiS\(_2\), and the 329 and 194 cm\(^{-1}\) modes in "PbTiS\(_3\)" [7,23]. The same behaviour has been observed in the LO phonon peak of PbS at 204 cm\(^{-1}\) [13].

Fig. 3. Typical dependencies of the frequencies \(\omega\) of "203" and "333" phonons (not shown for "412" and "632") of the misfit (PbS)\(_{1.18}\)(TiS\(_2\))\(_2\) on laser power (estimated at the sample surface) at T = 298 K from the data obtained with the 514.5 nm laser line. The symbols correspond to different series of experiments in the XX polarisation (for XY polarisation the dependencies were quite similar). The inset demonstrates both the softening of the wave number and the increase of its band area with real laser power on the sample (estimated in mW): 1, 0.7; 2, 1.3; 3, 2; 4, 2.7; 5, 4; 6, 6.
In the low-frequency region of the Raman spectra of the misfit (PbS)\textsubscript{1.18}(TiS\textsubscript{2})\textsubscript{2} previously unknown peculiarities have been revealed (Fig. 4, Table 1). Both bulk and thin solid film pieces of PbS single crystals exhibited the above features, so we related them to the PbS layers. According to the calculations of Upadhyaya et al., one may attribute the peaks at 19 and 95–96 cm\textsuperscript{-1} to LA(X) – TA(X) and LA(X) + TA(X) phonons in PbS [24].

The peak at 73 cm\textsuperscript{-1} in PbS was close to the 68 cm\textsuperscript{-1} TO(T) phonon established in PbS nanocrystals [19]. Notice that Hyngao et al. reported peaks at 41, 80, 194 cm\textsuperscript{-1} for (XX) and 41 cm\textsuperscript{-1} for (XY) polarisation geometries in the similar “PbTiS\textsubscript{3}” misfit [7]. The peaks at 80 and 194 cm\textsuperscript{-1} are close to ours (73 and 203 cm\textsuperscript{-1}). Earlier, forbidden first-order Raman spectra in PbS were already observed but only in a high frequency region (>100 cm\textsuperscript{-1}) [13, 25, 26]. The reasons of their manifestation are still unclear (Smith et al. proposed a Fröhlich resonance mechanism [13]). Presently it seems difficult to establish an exact origin of the low-frequency spectra we observed (Fig. 4).

Thus, the Raman spectra of the misfit were found in a first approximation to consist of individual interlayer vibrations of PbS and TiS\textsubscript{2} layers, with a possible superposition [9] phonon near 286.5 cm\textsuperscript{-1} (Fig. 1).

Under the significant increase of laser power the “oxidation” of (PbS)\textsubscript{1.18}(TiS\textsubscript{2})\textsubscript{2} misfit surface happened mainly by a way of formation of simple oxides such as PbO (140, 280) [27–29] and TiO\textsubscript{2} (140) [18] as well as PbSO\textsubscript{4} (434 and 605 cm\textsuperscript{-1}) [28, 29] at moderate laser powers (Fig. 2, curve 4, 5) and “PbO-PbSO\textsubscript{4}” complexes (254 and 434 cm\textsuperscript{-1}) (not shown in the figures) at higher energy densities. Thermal heating of the misfit surface under irradiation with laser beam, and, hence, the temperatures of formation of the oxides may be evaluated using the methods described, for example in Ref. [30]. According to the literature data, the above-mentioned oxides (as well as PbSO\textsubscript{4}) do not exhibit the wave numbers at 19 and 73 cm\textsuperscript{-1} [27, 29]. A laser beam of high power induced the irreversible local distortions of the crystal structure resulting in softening of “own” phonons in an irradiated point, and the phonon peaks at 203, 333, and 632 cm\textsuperscript{-1} we observed at 197–198, 325–327, and 625 cm\textsuperscript{-1}, respectively.

4. Conclusion

Thus, in the present work the Raman spectra of (PbS)\textsubscript{1.18}(TiS\textsubscript{2})\textsubscript{2} have been obtained in a range of 10–750 cm\textsuperscript{-1}. The established number of new phonons (19, 73, 95–96, 151, 362 cm\textsuperscript{-1}) in comparison with the similar misfits [7, 9–12] (Table 1) contributed to a corrected interpretation of the spectra, revealing so the Raman spectra of PbS layers and intercalation effect on TiS\textsubscript{2} phonons. A method of variation of laser power used permitted to observe a feature near ~151 cm\textsuperscript{-1} attributing to TA + TO superposition of PbS [13] in a region preceding the formation of oxide and oxysulfide complexes (PbO, TiO\textsubscript{2}, PbO\textsubscript{2}, PbSO\textsubscript{4}, and “PbO-PbSO\textsubscript{4}”), and therefore, permitted to distinguish the “own” and “oxidation” peaks.

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References