Optical properties of $PbTe_{0.95}S_{0.05}$ single crystal at different temperatures: far – infrared study

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Far – infrared spectroscopy over a wide temperature range was used to investigate vibration properties of $PbTe_{0.95}S_{0.05}$ single crystal. The analysis of the far infrared spectra was made by fitting procedure based on the model of coupled oscillators. Namely, we used dielectric function that in advance takes into account the existence of plasmon – two phonon interaction. As a result of the best fit we obtained three frequencies of coupled modes and than we calculated values for two LO modes and plasma frequencies (ω_P). We obtained a very good agreement between the result obtained as a best fit from experimental spectra and theoretical prediction. We have found that phonons in $PbTe_{0.95}S_{0.05}$ show the two – mode behavior.

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1. Introduction

The optical properties of lead telluride have been studied due to its interesting physical properties and applications for infrared optoelectronic devices. Its small band gap and high carrier mobilities identify it as a basic material for infrared optoelectronic devices [1] and thermoelectric materials in two – dimension quantum well systems [2]. Namely, lead – chalcogenides and their solid solutions have electrical active native point defects (vacancies and interstitial atoms) which produce energy states lying above the bottom of the conduction band (donor defects) or below the top of the valence band (acceptors) [3]. This leads to high charge carrier concentration in undoped crystals because of the deviation of composition from stochiometry. Furthermore, neither cooling nor magnetic field has been observed to have the freeze – out effect on charge carriers.

Absorption of electromagnetic radiation by free carriers is conditioned by their interaction with a lattice. Both individual carrier transitions and generation of collective plasma oscillators (plasmons) may contribute to this absorption. The coupling of elementary excitations in solids has been investigated by many authors [4 – 6]. The pseudo–binary alloy PbTe – PbS is interesting material for investigation in this field. $PbTe_{1-x}S_x$ is a narrow gap semiconductor with a direct gap in the infrared region [7]. Experimental studies [7, 8] indicate that there is a second – order phase transition in the $PbTe_{1-x}S_x$ system. Namely, the $PbTe_{1-x}S_x$ alloys may undergo a complex phase transition: a coupled orientational order – disorder and displacive ferroelectric phase transition (FTP), where the long – range ordering of dipoles created by off – center sulphur ions may induce the bulk displacive FPT [8]. Nevertheless, $PbTe_{1-x}S_x$ alloys cannot be treating simply by interpolating the phonon behaviour between two end – point materials. Far – infrared spectroscopy is a powerful technique for investigation in this field. In our paper, we presented far – infrared reflectivity spectra of $PbTe_{0.95}S_{0.05}$ single crystal sample.

2. Sample and experiment

Single crystal of $PbTe_{0.95}S_{0.05}$ alloys was grown by the vapour – liquid – solid (VLS) technique, using metal and chalcogenide atoms of high purity as the source materials. The details of the growth procedure can be found in [7]. The chemical composition of the sample was controlled by X–ray microprobe investigation. The structural characterization of the obtained sample was carried out by the XRD powder technique, using a Siemens D500 powder diffractometer with CuK_α, Ni – filtered radiation, in the diffraction angle range $2\theta = 25 – 100^o$.

Far – infrared reflection spectra were measured between 10 K and 300 K in the spectral range of 20 – 250 cm^{-1} on a BOMEM DA8 spectrometer.

3. Reflectivity analysis and fitting procedure

The low – frequency dielectric properties of PbTe and PbS might be interpreted with a frequency dependent dielectric function with not less then two classical oscillators ($n \geq 2$) corresponding to the TO – modes, superimposed by a Drude part that takes into account the free carrier contribution [9]:

$$\varepsilon_S(\omega)=\varepsilon_\infty+\sum_{k=1}^{n}\frac{\varepsilon_\infty\left(\omega_{LOk}^2-\omega_{TOk}^2\right)}{\omega_{TOk}^2-\omega^2-i\gamma_{TOk}\omega}-\frac{\varepsilon_\infty\omega_P^2}{\omega\left(\omega+i\gamma_P\right)} \quad (1)$$

where ε_∞ is the bound charge contribution and is considered as a constant, ω_{LOk} and ω_{TOk} are the longitudinal and transverse optical – phonon frequencies, ω_P is the plasma frequency, and γ_{TOk} and γ_P are the phonon and plasma damping. In the cases of PbTe and PbS, characteristically frequencies are ω_{LOPbTe} = 104 cm^{-1}, ω_{TOPbTe} = 32 cm^{-1}, ω_{LOPbS} = 216 cm^{-1} and ω_{TOPbS} = 66 cm^{-1}.

Thus the fit immediately yielded the TO mode frequencies. LO modes are determined by the maximum of the dielectric loss function. In PbTe system the pure LO – mode (ω_{LOPbTe}) of the lattice is strongly influenced by the plasmon mode (ω_P) of free carriers. As a result the combined plasmon – LO phonon modes ($\omega_{l1,l2}$) (n = 1) were observed [10]. In the experimental spectra only coupled mode positions are observable. Therefore the determination of LO – modes is connected with the decoupled procedure [11]. Heaving this in mind, in the analysis of reflectivity spectra of $PbTe_{0.95}S_{0.05}$ we have decided to use dielectric function, which takes into account existing of plasmon – phonon coupling in advance [11].

The lines in Fig. 1 are obtained using the dielectric function:

$$\varepsilon_f(\omega)=\varepsilon_\infty\frac{\prod_{j=1}^{m+1}\left(\omega^2+i\gamma_{lj}\omega-\omega_{lj}^2\right)}{\omega\left(\omega+i\gamma_P\right)\prod_{i=1}^{m}\left(\omega^2+i\gamma_{ti}\omega-\omega_{ti}^2\right)}\cdot$$

$$\prod_{p=1}^{l}\frac{\omega^2+i\gamma_{LOp}\omega-\omega_{LOp}^2}{\omega^2+i\gamma_{TOp}\omega-\omega_{TOp}^2} \quad (2)$$

The ω_{lj} and γ_{lj} parameters of the first numerator should be understood as the eigenfrequencies and damping coefficients of the coupled plasmons – m longitudinal phonon waves. The parameters of the first denominator correspond to the similar characteristics of the transverse (TO) vibrations. The second term in Eq. 2 represents l uncoupled modes of the crystal, where ω_{LOp} and ω_{TOp} are the longitudinal and transverse frequencies, and γ_{LOp} and γ_{TOp} corresponding damping. Also, $n = m + l$. Therefore, the determination of LO – mode and plasma frequency is connected with the decoupled procedure, which is the case for PbTe and PbS.

Situation, which considers coupling of one plasmon and one phonon, as it is the case for PbTe and PbS, is explained in detail in Ref. [11]. The coupled mode positions are defined as the solutions of a real part of Eq. 1(Re{ε_S} = 0), and they are given by:

$$2\omega_\pm^2=\omega_{LO}^2+\omega_P^2\pm\sqrt{\left(\omega_{LO}^2+\omega_P^2\right)^2-4\omega_P^2\omega_{TO}^2} \quad (3)$$

On that way, in principle, its $\omega_{lj}=\omega_\pm$ (j = 1, 2). The value of coupled plasmon – phonon modes were determined using fitting procedure, while the values of initial ω_{LOPbTe} and ω_P modes are determined by using the following equations:

$$\omega_P=\frac{\omega_{l1}\omega_{l2}}{\omega_t},$$

$$\omega_{LOPbTe}^2=\omega_{l2}^2-\omega_P^2\left[1-\left(\frac{\omega_t}{\omega_{l2}}\right)^2\right] \quad (4)$$

When we taking into account existence of this interaction in a case of $PbTe_{0.95}S_{0.05}$ alloys and than eliminated free carrier influence, we get the following values for LO phonon frequencies ω_{LO1} = 84 cm^{-1} and ω_{LO2} = 163 cm^{-1}. But, using Genzel's model [12] for the calculation of phonon frequencies in mixed crystals the ω_{LO1} = 108 cm^{-1} and ω_{LO2} = 155 cm^{-1} values are obtained. Therefore, we did not get satisfying result.

Considering this fact, in the analysis of reflectivity spectra of $PbTe_{0.95}S_{0.05}$ we have decided to use dielectric function that takes into account the existence of plasmon – two LO phonon interaction in advance. That corresponds to n = 2 in dielectric function given by Eq. (1). The coupled modes positions are defined as the solutions of a real part of the Eq. (1) (Re{ε_S} = 0). In this case there are three coupled modes, which can be calculated by solving the equations:

$$\omega^6-A\omega^4-B\omega^2-C=0, \quad (5)$$
$$A=\omega_{LO1}^2+\omega_{LO2}^2+\omega_P^2,$$
$$B=\omega_{LO1}^2\cdot\omega_{LO2}^2+\omega_P^2\left(\omega_{TO1}^2+\omega_{TO2}^2\right),$$
$$C=\omega_{TO1}^2\cdot\omega_{TO2}^2\cdot\omega_P^2$$

If we use the dielectric function defined by Eq. (2) the values of initial ω_{LO1}, ω_{LO2} and ω_P modes can be determined by:

$$\omega_P=\frac{\omega_{l1}\omega_{l2}\omega_{l3}}{\omega_{t1}\omega_{t2}},$$

$$\omega_{LO1,2}^2=\frac{1}{2}\left(\omega_{l1}^2+\omega_{l2}^2+\omega_{l3}^2-\omega_P^2\right)\pm$$
$$\sqrt{\left(\frac{1}{4}\left(\omega_{l1}^2+\omega_{l2}^2+\omega_{l3}^2-\omega_P^2\right)^2-\omega_{l1}^2\omega_{l2}^2-\omega_{l1}^2\omega_{l3}^2-\omega_{l2}^2\omega_{l3}^2+\omega_P^2\left(\omega_{t1}^2+\omega_{t2}^2\right)\right)} \quad (6)$$

The parameters adjustment was carried out automatically, by means of the least – square fitting of theoretical (R) and experimental (R_e) reflection coefficients at k arbitrary taken points:

$$\chi=\sqrt{\frac{1}{k}\sum_{j=1}^{k}\left(R_{ej}-R_j\right)^2}, \quad R=\left|\frac{\sqrt{\varepsilon}-1}{\sqrt{\varepsilon}+1}\right|^2 \quad (7)$$

when ε is given by Eq. (1) or Eq. (2). The value of χ was minimized until it become comparable with the usual experimental error. Practically for all samples the

determined errors of the eigenfrequencies and damping coefficients were about 3 – 6% and 10 – 15% respectively.

4. Results and discussion

The far – infrared reflection spectra of the $PbTe_{0.95}S_{0.05}$ single crystal sample are presented in Fig. 1. The experimental data are presented with circles, while the solid lines were obtaining using the dielectric function from Eq. (2). The oscillator of a weak intensity, at about 70cm^{-1} (denoted by * in Fig. 1), is a Brillouin zone edge mode, because the phonon density of PbTe has a maximum at these frequencies [13].

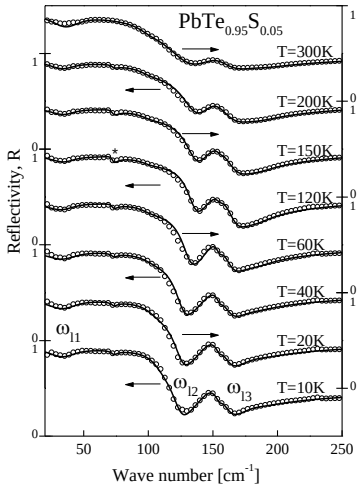

Fig. 1. Far – infrared reflection spectra of $PbTe_{0.95}S_{0.05}$ single crystal. Experimental spectra are presented by circles. The solid lines are calculated spectra obtained by a fitting procedure based on the model given by Eq. (2).

As a result of the best fit we obtained the frequencies of coupled modes (ω_{l1}, ω_{l2}, and ω_{l3}), marked in Fig. 1, and then calculated the values for ω_{LO1}, ω_{LO2} and ω_P, as it is described in the Sec. 3. The characteristic parameters obtained in this way are shown in Fig. 2.

In Fig. 2, the point (+) refers to the eigenfrequency spectra ω_{lj} obtained by Eq. (2). The solid lines in Fig. 2 are obtained by the application of Eq. (5). The agreement of the plasmon – two LO phonon mode frequencies calculated in such a way, with the experimentally determined ones is very good. The open circles in Fig. 2 represent the calculated values for ω_{LO1}, ω_{LO2} and experimentally determined values for ω_{TO1} and ω_{TO2}. Values determined in this way are in excellent agreement with calculated values based on the Genzel's model [12], mentioned above. The obtained results presented in Fig. 2. is the best demonstration of the fact that use of the dielectric function given by Eq. (2) is justifiable. Also, the results shown in Fig. 2 suggest that the optical phonons in $PbTe_{1-x}S_x$ mixed crystals have a well – known two – mode behavior (each TO – LO mode pair of the end members degenerates to an impurity mode), according to Genzel's notation [12].

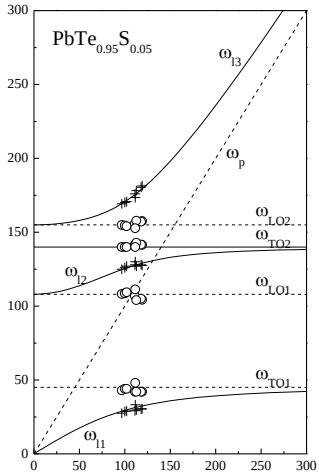

Fig. 2. The eigenfrequencies of the plasmon – two LO phonon modes (full lines – Eq.5); points (+) refer to the eigenfrequency spectra ω_{lj} obtained by Eq. (2); the open circles (o) represent calculated values for ω_{LOi} and experimentally determined values for ω_{TOi}.

5. Conclusion

As a method to investigate phonon properties of $PbTe_{0.95}S_{0.05}$ single crystal we used the far – infrared spectroscopy. In the analysis of far infrared spectra of $PbTe_{0.95}S_{0.05}$ at different temperatures we used dielectric function that in advance takes into account the existence of plasmon – two phonon interaction. As a result of the best fit we obtained three frequencies of coupled modes (ω_{l1}, ω_{l2}, and ω_{l3}), and than we calculated values for two LO modes (ω_{LO1} and ω_{LO2}) and plasma frequencies (ω_P). In spite of the strong plasmon – two LO phonon interaction, we found that long wavelength optical phonon modes of these mixed crystals show a two – mode behavior.

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