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FAR INFRARED CHARACTERIZATION OF SAMARIUM DOPED SINGLE CRYSTAL PbTe

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Single crystal samples of lead telluride doped with samarium were produced using the Bridgman method. Far infrared reflectivity spectra in the temperature range 10 K - 300 K are presented and numerically analyzed using a fitting procedure based on a modified plasmon-phonon interaction model. The optical parameters were determined and three local modes of samarium were observed at about 167 cm^{-1}, 227 cm^{-1} and 486 cm^{-1}.

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1. Introduction

Lead telluride, PbTe, is a very well known semiconductor used in optoelectronics [1]. Doping of PbTe with various impurities has been studied in the last twenty years. The strong influence of impurities, usually less than 0.5 at%, was associated with Fermi level pinning, persistent photoconductivity [2, 3] etc. It was recently shown that a substantial difference exists in the Fermi level pinning effect in PbTe doped with Yb compared to the cases when PbTe was doped with some group III impurities such as In, Ga or B [4]. The position of the pinned Fermi level depends on the concentration of ytterbium [5] while it does not depend on the amount of indium. A giant negative magnetoresistance effect in PbTe doped with Yb was observed [6]. Behavior of other rare-earth impurities in PbTe is studied less. The Hall coefficient, thermoelectric power and electrical conductivity in PbTe doped with La, Pr, Sm and Gd were ivestigated in the temperature range between 77 K and 300 K [7]. It was concluded that impurity atoms act as donors with an electrical activity that increases with temperature until the fraction of electrically active lanthanide atoms reaches values close to or slightly more than half of their total number. A monotonic decrease in the lattice constant with atomic number of the rare-earth metal takes place except for Eu, Tm and Yb in the telluride series. These four rare-earth elements tend to be in the +2 valence state whereas the other rare-earth elements are in the +3 valence state. As far as we know the far infrared optical properties has been measured only in the case when PbTe was doped with cerium [8].

In this work far infrared optical properties of PbTe doped with rare-earth element- samarium are presented. Reflectivity of single crystal samples was measured in the temperature range between 10 K and 300 K and the experimental results were numerically analyzed. The carrier concentration and their mobility were also measured at room temperature.

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2. Experimental

Single crystal ingots of PbTe doped with the starting composition of 3 at% Sm were synthetized using the standard Bridgman technique [9]. The composition of Sm increased from the top to the end along the length of the ingot so a number of samples with different content of samarium were cut and polished and then used for measurements.

Far infrared reflectivity measurements were made at temperatures between 10 K and 300 K using a Bruker IFS-113 V spectrometer equipped with an Oxford Instruments cryostat. Free carrier concentration and their mobility were measured at room temperature using the Van der Pauw method.

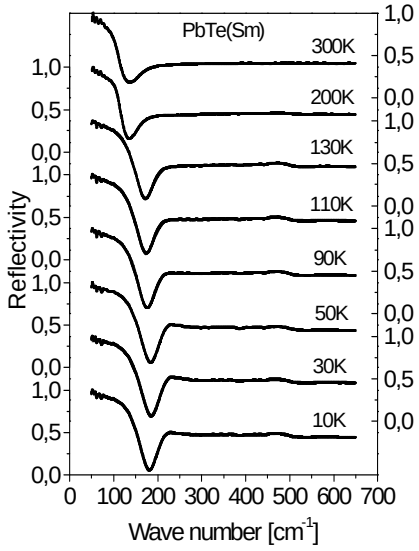

Fig 1. FIR reflectivity spectra of PbTe+0.5% Sm at different temperatures.

3. Results and discussion

Far infrared reflectivity spectra of single crystal PbTe doped with about 0.5 at % Sm are shown in Fig. 1. A well evidenced plasma minimum is observed at all temperatures, which was the sharpest at the lowest temperature (10 K). Two relatively small dips were observed for all temperatures below room temperature at about 380 cm^{-1} and 440 cm^{-1}. At present, these dips can be supposed to appear due to the effect of a thin layer of TeO_2 formed at the surface of the sample. At low temperatures two maxima of the reflectivity, at about 230 cm^{-1} and 486 cm^{-1}, are also observed which, in our opinion, are associated with the impurity, e.g. samarium.

All experimental diagrams were numerically analyzed using the following equation:

$$\varepsilon(\omega)=\varepsilon_{\infty}\frac{\prod_{j=1}^{2}(\omega^2+i\gamma_{lj}\omega-\omega_{lj}^2)}{\omega(\omega+i\gamma_p)(\omega^2+i\gamma_t\omega-\omega_t^2)}\prod_{n=1}^{p}\frac{(\omega^2+i\gamma_{Ln}\omega-\omega_{Ln}^2)}{(\omega^2+i\gamma_{on}\omega-\omega_{on}^2)}\prod_{k=1}^{q}\frac{(\omega^2+i\gamma_{LO}\omega-\omega^2{}_{LO})}{(\omega^2+i\gamma_{TO}\omega-\omega_{TO}^2)} \quad (1)$$

where ω_j and γ_j are parameters of the first numerator representing the eigenfrequencies and damping factors of plasmon-longitudinal phonon waves, respectively. Parameters of the first denominator correspond to transversal (TO) vibrations while γ_p is the damping factor of plasma. The second term in Equation (1) represents the impurity local modes where ω_{01} and ω_{02} are characteristic impurity mode frequencies. Frequencies ω_{L1} and ω_{L2} are parameters connected with the oscillator strength (S) and γ_{01}, γ_{02}, γ_{L1} and γ_{L2} are their damping factors, respectively. Finally, ω_{LO} and ω_{TO} are the longitudinal and transversal frequencies, and γ_{LO} and γ_{TO} stand for the damping factors of uncoupled modes of the host crystal. Best fit values of these parameters were calculated.

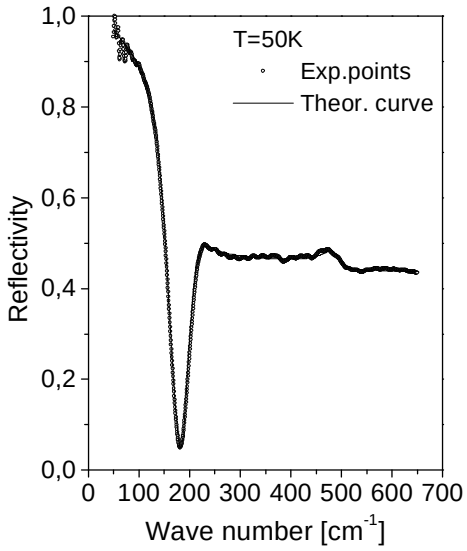

Fig. 2. FIR spectrum of PbTe doped with about 0.5% Sm, measured at T=50 K. The experimental spectrum is denoted by with circles. The solid line is the calculated spectrum obtained by a fitting procedure based on the model given by Eq. (1).

The oscillators denoted by *j=1,2* in Equation (1) are dominant structures in the far infrared reflection spectra and represent the position of the coupled plasmon-LO phonon modes. The frequency of mode ω_{l1} [10] is marked by an arrow in Fig. 2 for the temperature of 50 K. The points show the experimental values while the solid line shows the results of numerical optimization of the parameters using Eq. (1). The reflectivity spectra were observed down to 50 cm^{-1}, so the value of 32cm^{-1} for the transversal phonon frequency ω_t is taken from literature [11].

Oscillators of weak intensities at about 50 and 70 cm^{-1} are modes from the edge of the Brillouin zone because the phonon density of PbTe has a maximum at these frequencies [12], while the mode at 105 cm^{-1} represents the LO mode of PbTe (the third term in Eq. (1)). The values for ω_p were determined using the following equation [10] :

$$\omega_p = \frac{\omega_{l1}\omega_{l2}}{\omega_t} \tag{2}$$

The values of all parameters calculated using equations (1) and (2) are given in Table 1. They were calculated from a least squares fit to the experimental reflectivity data.

The calculated values of plasma frequencies versus temperature are given in Fig. 3. The plasma frequency increases as the temperature decreases from 300 K to 110 K and then is almost constant going down to 10 K. This is the consequence of the change in the free carrier's concentration in PbTe doped with Sm, when the Fermi level is pinned. High frequency dielectric permittivity ε_∞ decreases when the temperature increases from 10 K to about 90 K and becomes an almost constant- room temperature value (Fig. 4). Looking at the reflectivity diagrams in Fig. 1 and Fig. 2 one can see that for low temperatures reflectivity has two levels, one a bit lower for frequencies above 500 cm^{-1} and a slightly higher level between 250 cm^{-1} and 450 cm^{-1}. At frequencies of about 230 cm^{-1} and 480 cm^{-1} there are two broad maxima which could perhaps be associated with local modes of impurity- samarium. But here one could also take into account that one relatively sharp peak was observed for PbTe doped with Ce also at about 230 cm^{-1} (Fig. 5). That peak was regarded to be a thin layer of frozen water at the sample surface when the evacuation of the cryostat chamber was insufficiently high. This is in agreement with the experimental results of Warren [13]. We proposed the existence of two local modes at about 227 cm^{-1} and also about 486 cm^{-1} in Table 1. Besides that we determined an oscillator frequency at about 167 cm^{-1}.

Table 1. The values of the optical parameters calculated using equations (1) and (2).

Paramet.	*10 K*	*30 K*	*50 K*	*90 K*	*110 K*	*130 K*	*200 K*	*300 K*
ω_p (cm^{-1})	168.9	167.6	167.8	166.5	164.1	161.1	148.9	133.53
ε_∞	35.6	33.7	34.6	33.0	33.6	33.0	33.3	32.6
ω_{t1}	194.6	188.2	184.5	187.3	178.8	175.6	160.76	142.7
γ_{t1}	29	25	23	49	63	89	29	38
ω_{t2}	16.05	18.1	20.1	22.4	23.96	26	28.35	30
γ_{t2}	4×10^{-8}	1×10^{-4}	1.23×10^{-4}	2.22	6.9×10^{-5}	1.28	1.6×10^{-6}	1.62
ω_t	18.49	20.33	22.1	25.2	26.1	28.35	30.61	32.1
ω_{L1}	235.1	229.3	230.4	226.5	228	228.7	228.2	228.5
γ_{L1}	2307	2039	1186	1500	3036	2272	1112	389
ω_{01}	227.4	224.7	220.1	219.4	219	219.7	217	217.5
γ_{01}	32	38	43	39	52	62	99	180
ω_{L2}	517.2	488.9	490.4	495	491.9	491.7	492	491.5
γ_{L2}	299	27	45	82	66	56	68	4
ω_{02}	486.3	486.7	486.9	486.5	486	485.7	486.6	486.4
γ_{02}	274	25	39	72	59	49	60	1×10^{-3}
ω_{L3}	173.2	170	170	170.8	170.4	170	170.4	170
γ_{L3}	35	44	45	28	28	26	148	126
ω_{03}	167.9	167.1	167.1	167.1	167.1	167.1	167.1	167.1
γ_{03}	267	468	337	401	908	879	1137	109
ω_{LO} *(PbTe)*	105	105	105	104.7	104.7	104	105	105
γ_{LO} *(PbTe)*	344	1130	594	429	1081	642	315	209

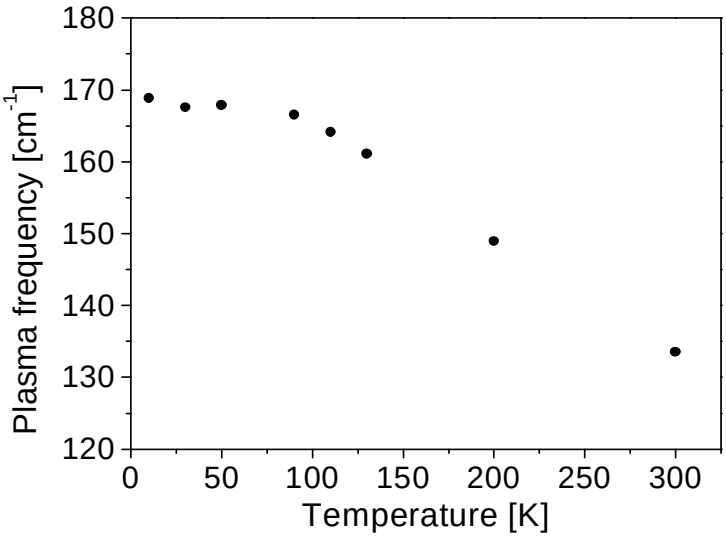

Fig. 3. The change of plasma frequency versus temperature for PbTe(Sm).

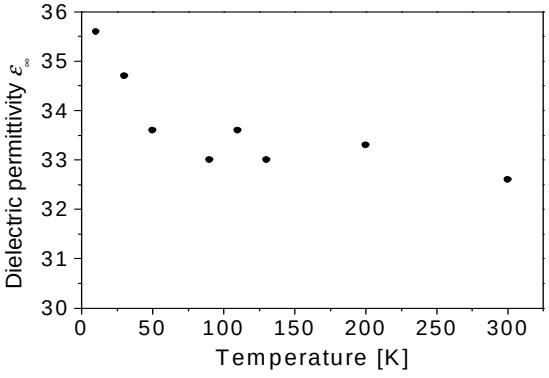

Fig. 4. High frequency dielectric permittivity versus the temperature between 10 K and 300 K.

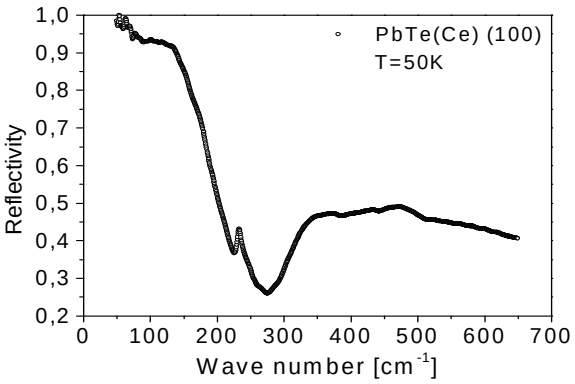

Fig. 5. FIR spectrum of PbTe doped with about 0.5 At% Ce measured at 50 K.

These results are compable with literature data for PbTe doped with another rare earth element-ytterbium (Yb) which, similarly to Sm, also has two electrons in *5s* and *6s* shells and six electrons in the *5p* shell. While Yb has the maximum number of electrons (fourteen) in the *4f* shell, Sm only has six electrons. In both Sm and Yb the source of ionization of electrons are not *5s* and *5p* orbits. The source of ionization are at $4f^6 6s^2 (^8F_0)$ levels in Sm and $4f^{14} 6s^2 (^1S_0)$ in Yb. This means that *5s* and *5p* shells are above the *4f* one. For one-fold ionization of the Sm atom it is $4f^6 6s (^8F_{1/2})$, for two-fold it is $4f^6 (^7F_0)$ and for three-fold ionization it should be $4f^5 (^6H_{5/2})$. For Yb it is similar as for one-fold ionization $4f^{14} 6s (^2S_{1/2})$, for two-fold $4f^{14} (^1S_0)$ and for three-fold ionization it is $4f^{13} (^2F_{1/2})$. The ionization potential of atoms is also similar for these two elements. For Sm it is 5.6eV, 11.4eV and 24.0 eV, while for Yb it is 6.22 eV, 12.1 eV and 25.61 eV, respectivelly.

Now it would be important to consider which state exists for our observed Sm local modes: Sm^+, Sm^{2+} or Sm^{3+}. The position of the pinned Fermi level for PbTe doped with Yb is defined by the balance between the Yb^+ and Yb^{3+} dopant charge [14, 15]. The electron state Sm^+ should be a more stable than the electron states Sm^{2+} and Sm^{3+}. Thus we suppose that Sm behaves similarly to elements of the IIIA group when PbTe was doped with In or B. That means that Sm^{2+} state may transfer to a more stable form as follows [16]:

$$2Sm^{2+} = Sm^+ + Sm^{3+}$$

and the electron from the Sm^+ state may transfer to the conduction band

$$Sm^+ = Sm^{3+} + 2e^-.$$

The position of the pinned Fermi level depends on the balance between Sm^+ and Sm^{3+}.

The free carrier concentration of our sample, PbTe doped with Sm, was measured at room temperature and it was $p = 2.56 \times 10^{17} cm^{-3}$ with a mobility of 1467 cm^2/Vs. Knowing that mobility of holes in pure PbTe is about 750 cm^2/Vs this measurement confirmed that the sample doped with Sm has improved properties. It is also interesting to mention that PbTe doped with another rare earth element- ytterbium produces a “giant negative magnetoresistance effect in PbTe” [6]. We feel that it is worthwhile to continue this type of investigation on PbTe doped with Sm.

5. Conclusion

In this work the far-infrared reflection spectra of PbTe doped with Sm single crystal at temperatures between 10 K and 300 K has been shown. Besides a strong plasmon-LO phonon interaction three additional modes, at about 167 cm^{-1}, 227 cm^{-1} and 486 cm^{-1}, at temperatures below 200 K were observed. We believe that two of them, at 167 cm^{-1} and 227 cm^{-1}, belong to the impurity effect of Sm. The third mode, we believe, belongs to a phase transition.

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