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Far infrared study of some rare earth impurities in crystals of $Pb_{1-x}Sn_x$ alloys

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Single crystal samples of $Pb_{0.9}Sn_{0.1}Te$ doped with Yb, Sm or Gd were produced using the Bridgman method. Far infrared reflectivity spectra were measured at room temperature for highly polished samples with various impurity concentration (between 0.2 at% and 1 at %). The experimental diagrams were numerically analyzed using a fitting procedure based on the plasma-phonon interaction model and the optical parameters were determined. The application of lead- tin tellurides doped with rare earth elements for infrared astronomy has been discussed.

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1. Introduction

An interesting class of far infrared photodetectors based on lead-tin tellurides doped with group III impurities is well known [1,2]. There the Fermi level becomes pinned at a stable position. Also a persistent photoconductivity effect in $Pb_{1-x}Sn_xTe$ doped with In is registered due to a strong electron – lattice coupling in the system. Recently the persistent photoconductivity effect was observed for lead- telluride doped with Ytterbium [3]. So, again PbSnTe doped with rare-earth elements is becoming interesting as a possible group of semiconductors for the production of far infrared high-performance PbSnTe-based detectors. Lead telluride doped with rare earth elements has been investigated for some time [4] with potential advantages of certain elements as n-type dopants for lead chalcogenides diode lasers grown by molecular beam epitaxy. Donor like behavior of rare earth impurities in PbTe was studied more recently [5] where the change of free carriers mobility and Seebeck coefficient in PbTe doped with La, Pr, Sm or Gd were interpreted by invoking a band of impurity resonant status. The nature of the donor action of Gd impurity in crystals of lead and tin telluride was also studied [6].

In this work, far infrared reflectivity spectra of $Pb_{0.9}Sn_{0.1}Te$ doped with Sm, Gd or Yb were measured at room temperature and numerically analyzed enabling a comparison of the influence of small amounts of different rare earth dopants on the determined free carrier mobility values.

2. Experimental

Single crystals of $Pb_{0.9}Sn_{0.1}Te$ doped with a starting composition of 2 at% Yb, Sm or Gd were produced using the Bridgman method [7]. High purity elements (6N) Pb, Sn and Te were used as the source material and (3N) for Yb, Sm and Gd. It was found that along the ingot the concentration of all three impurities increased from the top to the end of each ingot. The contents of each element were determined using EDS analysis. Far infrared reflectivity spectra were measured using a Bruker IFS 113 V spectrometer.

3. Experimental results and discussion

The room temperature reflectivity diagrams as a function of the wave number, for single crystal PbSnTe samples doped with (a): 0.7 at%Sm and (b): 0.2 at%Sm are given in Fig. 1.

For these two diagrams a plasma minimum was observed at about 235 cm^{-1} and 330 cm^{-1}, respectively. Here it was obvious that the plasma minimum moves towards a higher wave number when the content of Sm is lower.

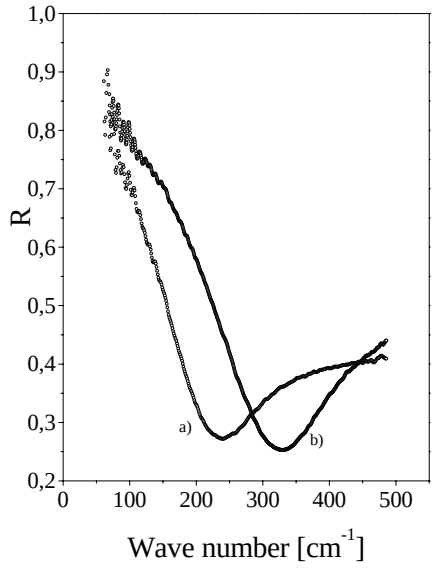

Fig. 1. The room temperature reflectivity diagrams of single crystal PbSnTe samples doped with (a) 0.7 at%Sm and (b) 0.2 at%Sm.

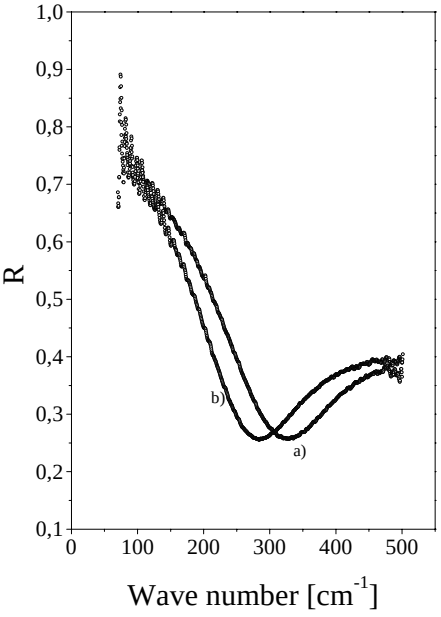

Fig. 2. The room temperature reflectivity doped with (a) 0.3 at%Gd and (b) 0.8 at%Gd diagrams of single crystal PbSnTe samples.

Similar was noted when PbSnTe was doped with Gd. Fig. 2 shows two reflectivity diagrams, the first (a) for PbSnTe doped with about 0.3 at% Gd which has a plasma minimum at about 330 cm^{-1} and the second one (b) with a higher impurity concentration ($\approx 0.8 at\%Gd$) where the plasma minimum is at a lower wave number ($\approx 280 cm^{-1}$).

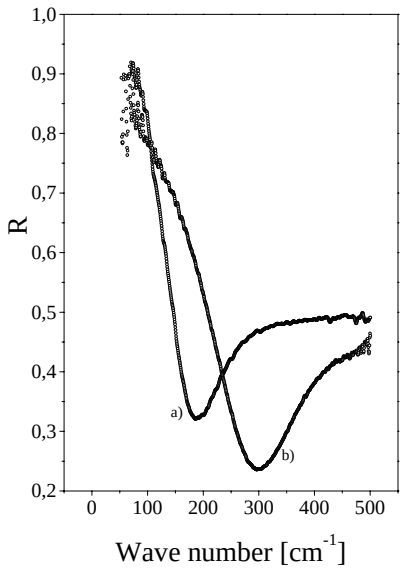

Fig. 3. The room temperature reflectivity diagrams of single crystal PbSnTe samples doped with 0.2 at%Yb and (b) 0.6 at%Yb

When PbSnTe was doped with Yb it was contrary. For a sample doped with 0.2 at% Yb the plasma minimum was at about 180cm^{-1} while for the sample with about 0.6 at% Yb the plasma minimum was at about 300cm^{-1}. That is shown in Fig. 3.

Generally speaking, one can even now notice that our PbSnTe samples doped with all three rare earth elements have plasma minima at rather low frequencies compared with undoped literature PbSnTe samples [8].

All experimental results were numerically analyzed using a modified four parameter model for the dielectric function [9] which takes into account that in our case the pure longitudinal –LO modes of the lattice are strongly influenced by the plasma mode of the free carriers [10].

$$\varepsilon(\omega) = \varepsilon_\infty \frac{\prod_{j=1}^{2}(\omega^2 + i\gamma_{lj}\omega - \omega_{lj}^2)}{\omega(\omega + i\gamma_p)(\omega^2 + i\gamma_t\omega - \omega_t^2)} \cdot \prod_{n=1}^{r} \frac{(\omega^2 + i\gamma_{Ln}\omega - \omega_{Ln}^2)}{(\omega^2 + i\gamma_{0n}\omega - \omega_{0n}^2)} \cdot \prod_{k=1}^{q} \frac{(\omega^2 + i\gamma_{LOk}\omega - \omega_{LOk}^2)}{(\omega^2 + i\gamma_{TOk}\omega - \omega_{TOk}^2)} \quad (1)$$

The ω_{lj} and γ_{lj} of the first numerator represent the eigenfrequencies and damping factors, respectively of longitudinal plasmon LO phonon waves, which arise as a result of the interaction of initial modes. The parameters of the first denominator correspond to transversal (TO) vibrations, while γ_p is the damping factor of plasma. ε_∞ is the dielectric high frequency permittivity. The second term in the Eq.(1) refers to the impurity modes, where ω_{0n} and ω_{Ln} are characteristic transverse and longitudinal wave numbers, respectively; γ_{0n} and γ_{Ln} are

their damping factors; ω_{LOk} and ω_{TOk} are the longitudinal and transverse wave numbers and γ_{LOk} and γ_{TOk} are the damping factors of uncoupled modes the host crystal.

Reflectivity spectra were observed down to 50cm^{-1} so the transversal phonon mode ω_t at room temperature was taken from literature [11] to be 32cm^{-1}. The plasma wave numbers were determined using the following equation [10]:

$$\omega_p = \frac{\omega_{l1} \cdot \omega_{l2}}{\omega_z} \ldots \quad (2)$$

The starting values of all parameters, for the fitting procedure were previously determined using Kramers-Krönig analysis. The starting values of ε_∞ were calculated using the equation

$$\varepsilon_\infty = \left[\frac{1+\sqrt{R_\infty}}{1-\sqrt{R_\infty}}\right]^2 \ldots. \quad (3)$$

Where R_∞ is the experimental value of reflection coefficient on the upper limit of the wave number measured interval. As an example a fitted curve for FIR spectrum of sample PbSnTe doped with 0.22 at% Yb is given in Fig. 4.

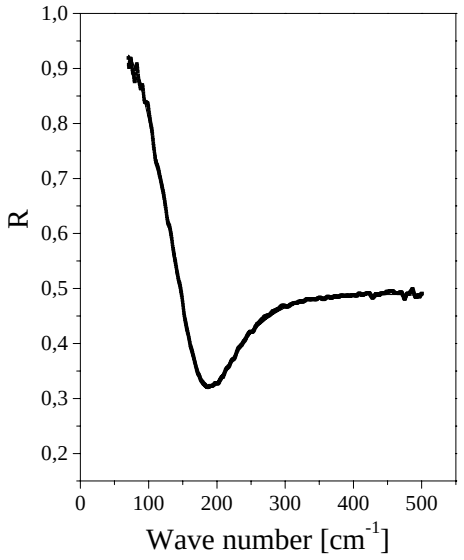

Fig. 4. Fitted curve for FIR spectrum of sample PbSnTe doped with 0.2 at% Yb. The full line is the fitted curve.

The optical free carrier mobility for all studied samples of PbSnTe doped with Sm, Gd and Yb were calculated using the method of Moss et al [12] and are given in Table 1.

Table 1. The optical free carrier mobility for samples of PbSnTe doped with Sm, Gd and Yb

PbSnTe sample doped with	0.2at %Sm	0.7at% Sm	0.3at% Gd	0.8at% Gd	0.2at% Yb	0.6at% Yb
$\omega_p(cm^{-1})$	298	213	310	251	170	274
$\mu_p[cm^2/Vs]$	400	778	487	600	937	585

Looking at Table 1, one can see that the samples with the higher concentration of Sm and Gd (0.7at%Sm and 0.8at%Gd, respectively) have the lowest plasma frequency at 213cm^{-1} for Sm and at 251 cm^{-1} for Gd. On the contrary when PbSnTe was doped with 0.6at% and 0.2at%Yb the plasma frequency decreased from 274cm^{-1} to 170cm^{-1}. For all samples from Table 1 the values of optical free carrier mobility were higher for lower values of plasma frequency. The results from Table 1 could be compared with literature data for pure PbSnTe alloy [8] where room temperature free carrier optical mobility is only about 300cm^{-1}. This means that the quality of our PbSnTe samples doped with all three rear-earth elements: Yb, Sm and Gd was improved significantly. The reason for similar behavior of these three rare earth impurities in PbSnTe should be very similar electronic structure of ionized states between Sm, Gd and Yb which is shown in Table 2. The sources of ionization of these three elements are not 5s and 5p orbits. They are at $4f^6 6s^2$ in Sm, $4f^7$ and $4f^{14}$ in Gd and Yb respectively. Beside that, 5s and 5p shells are above the 4f ones.

Table 2. Electronic structure of ionized states of Sm, Gd and Yb.

El.	Nonionized	e^{+1}	e^{+2}	e^{+3}
Sm	$4f^6 6s^2(^7F_0)$	$4f^6 6s(^8F_{1/2})$	$4f^6(^7F_0)$	$4f^5(^6H_{5/2})$
Gd	$4f^7 5d6s^2(^9D_2)$	$4f^7 5d6s(^{10}D_{5/2})$	$4f^7 5d(^9D_2)$	$4f^7(^8D_{7/2})$
Yb	$4f^{14} 6s^2(^1S_0)$	$4f^{14} 6s(^2S_{1/2})$	$f^{14}(^1S_0)$	$4f^{13}(^2F_{7/2})$

So, when the lead-tin tellurides are doped with rare earth element in a concentration exceeding the concentration of the other impurities, N_{imp}, the Fermi level becomes pinned at some definite position. This phenomenon is usually due to the energy band modulation. There are several theoretical approaches which can help in understanding the nature of impurity states in PbSnTe

alloys. For instance Ahmad et al recently considered the problem of deep defect states (DDS) in narrow band gap semiconductors with large electronic permittivity such as PbTe [13, 14]. Ahmad et al. [15] also studied the electronic structure of defects in PbTe which could help in further consideration of energy states of rare earth ions in narrow-gap PbSnTe semiconductors. One should also mention one previous paper about mixed-valence state in narrow-gap IV-VI semiconductors with rare earth ions [16] which could also help in studying this problem. It has been shown in the literature [17] that application of lead-tin tellurides doped with the group III impurities as base elements for the infrared photodetectors gives an important opportunity to produce universal and sensitive systems which have a number of advantageous features. Similarly, relatively high density of impurity photodetectors based on PbSnTe doped with rare earth would produce high stability of these devices with respect to the action of hard radiation, for example in infrared astronomy.

4. Conclusion

In this work, as far as we know, for the first time far infrared reflectivity spectra of single crystals $Pb_{0.9}Sn_{0.1}Te$ doped with various percentages of Sm, Gd and Yb were measured. The experimental spectra were numerically analyzed and it was shown that at room temperature optical free carrier mobility was several times higher compared with the literature data for pure PbSnTe alloys. This means that PbSnTe doped with an optimal concentration of rare earth could be used for production of infra red detectors in modern astronomy with improved characteristics.

References

[1] S. N. Chesnokov, D. E. Dolzhenko, I. I. Ivanchik, D. R. Khokhlov, Infrared Phys.Technol. **35**, 23 (1994)
[2] D. R. Khokhlov, I. I. Ivanchik, S. N. Raines, D. M. Watson, J. L. Pipher, Applied Phys. Lett. **76**, 2835 (2000)
[3] P. M. Nikolic, D. Lukovic, S. S. Vujatovic, K. M. Paraskevopoulos, M. V. Nikolic, V. Blagojevic, T. T. Zorba, B. Stamenovic, W. König, J. Alloys Compd. **466**, 319 (2008).
[4] D. L. Partin, J. Appl. Phys. **57**, 1997 (1985).
[5] G. T. Alekseeva, M. V. Vedernikov, E. A. Gurieva, P. P. Konstantinov, L. V. Prokofeva, Yu. I. Ravich, Semiconductors **32**, 716 (1998).
[6] D. M. Zayachuk, O. A. Dobrynskii, Semiconductors **32**, 1185 (1998).
[7] B. A. Akimov, A. V. Dimitriev, D. R. Khokhlov, L. I. Ryabova, Phys. Status Solidi A **137**, 9 (1993).
[8] G. Dionne, J.C. Wooley, Phys. Rev. B. **6**, 3898 (1972) .
[9] F. Gervais, B. Piriou, Phys. Rev. B **10**, 1642 (1974).
[10] A. A. Kukharski, Solid State Commun. **13**, 1761 (1973).
[11] N. Romcevic, J. Trajic, T. A. Kuznetsova, M. Romcevic, B. Hadzic, D.R. Khokhlov, J. Alloys Compd. **442**, 324 (2007).
[12] T. S. Moss, T. D. F. Howkins, G. J. Burell, J. of Phys. C 1435 (1968).
[13] S. Ahmad, K. Hoang, S. D. Mahanti, Phys.Rev.Lett. **96**, 056403 (2006).
[14] K. Hoang, S.D. Mahanti, Puru Jena, Phys. Rev. B **76**, 115432-1 (2007).
[15] S. Ahmad, S. D. Mahanti, K. Hoang, M. Kanatzidis, Phys. Rev. B **74**, 155205-1 (2006).
[16] V. K. Dugaev, V. I. Litvinov, A. Lusakowski, Phys. Rev. B **59**, 15190 (1991-I).
[17] D. Khokhlov, Int. J. Mod. Phys. B **18**, 2223 (2004).

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