

## FAR INFRARED AND TRANSPORT PROPERTIES OF SINGLE CRYSTAL PBTE SAMPLES DOPED WITH Ce

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Single crystal samples of lead telluride doped with cerium were made using the Bridgman technique. Single crystals could be easily cleaved parallel to the (002) plane. Room temperature far infrared reflectivity was measured on single crystal samples and a plasma minimum at about  $180\text{ cm}^{-1}$  and local modes of Ce were observed. A fitting procedure based on a modified four parameter model of plasmon – phonon interaction, was used to determine the values of optical parameters. Carrier concentration and their mobility were measured at room and liquid nitrogen temperatures.

*Keywords:* Lead Telluride, Ce-doping, Infrared Properties

### 1. Introduction

Lead telluride and its alloys were the subject of intensive research more than thirty years ago. Nikolić (1965, 1967) [1, 2] then observed that when PbTe was alloyed with SnTe the energy gap decreased having a positive temperature coefficient [3]. These alloys soon afterwards were used for producing infrared detectors and lasers for, until that time, an uncovered second atmospheric window ( $\lambda = 8\text{-}13.5\ \mu\text{m}$ ). These infrared detectors were used for more than one decade and then were replaced with  $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$  devices.

Later on Akimov et al. [4, 5, 6] first observed that when PbTe compounds and alloys are doped with some group III elements various effects appear which were not observed in pure lead telluride. For instance, the Fermi level becomes pinned at some stable position, which does not depend on the dopant concentration [7]. When the Fermi level pinning effect is present then the electrical properties of that semiconductor are quite homogenized. For instance for PbTe doped with In up to 50 periods of Shubnikov-de Haas (SdH) oscillators were resolved [8] that is the consequence of a very high degree of sample homogeneity.

A persistent photoconductivity effect was also observed [6, 9]. That is characteristic for DX-centers in some II-VI and III-V semiconductors. The appearance of DX-centers in these narrow gap semiconductors is not expected.

Besides these fundamental reason for this investigation, it is interesting to say, that the application of IV-VI semiconductors, doped with group III impurities is very promising for producing infrared detectors with very high stability and sensitivity.

The mentioned DX like behavior of lead telluride based alloys doped with group III impurities was recently extended to another group of dopants – rare earth. Skipetrov et al. [10] reported that they observed positive persistent photoconductivity and Fermi level pinning effects for  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  alloys doped with Yb. More recently the same effects were observed for PbTe doped with Yb by Ivanchik et al. [11]. It is also expected that when PbTe is doped with one rare earth element its parameters can be tuned with an external magnetic field.

In this work we have introduced another rare earth dopant – Ce in lead telluride. Single crystal samples were produced and some of their transport and far infrared properties have been examined.

## 2. Experimental results

A single crystal ingot of PbTe doped with 3 at.% Ce was grown using the classical Bridgman method. Using x-ray analysis it was confirmed that the PbTe +Ce ingot was a complete single crystal, which was easily cleaved parallel to the c-axis (200). Plates between 1 mm and 2 mm were obtained in this way with a shiny and parallel surface. Freshly cleaved samples were used for reflectivity measurements. Far infrared reflectivity measurements were done at room temperature using a Bomem Fourier Transform Spectrometer in the Institute of Physics, Belgrade University. In Fig. 1 a far infrared spectrum for a typical PbTe sample doped with Ce is given. We do not yet know the factor of segregation of cerium in PbTe so it is obvious that the content of cerium in each cleaved plate can be different, depending on how far the plates were cleaved from the beginning of the ingot.

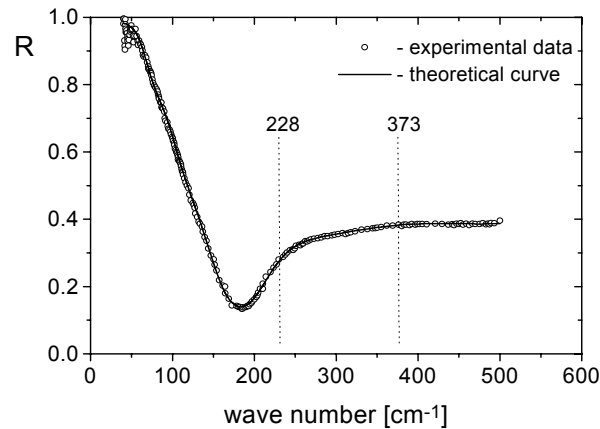


Fig. 1. Far infrared reflectivity room temperature spectrum of PbTe single crystal doped with cerium; Experimental results are represented with circles; The solid line is the calculated spectrum obtained by a fitting procedure.

The EDS method will be used to determine the content of cerium in each sample. That work is in progress. This method will also enable determination of the factor of segregation of Ce in PbTe.

Carrier concentration and mobility were measured at room and liquid nitrogen temperatures using the Van der Pauw method. The obtained values for free hole concentration,  $p$ , their mobility,  $\mu_p$  and resistivity,  $\rho$ , are given in Table 1.

Table 1. Transport properties for a typical PbTe + Ce sample at room and liquid nitrogen temperatures.

T [K]	thickness [mm]	$\rho$ [ $\Omega\text{m}$ ]	$p$ [ $\text{cm}^{-3}$ ]	$\mu$ [ $\text{cm}^2/\text{Vs}$ ]
300	1.5	$1.03 \times 10^{-4}$	$1.1 \times 10^{18}$	563
77	1.5	$1.7 \times 10^{-6}$	$3.1 \times 10^{18}$	6360

### 3. Discussion

The experimental room temperature reflectivity diagram, given in Fig. 1 is shown with circles while the full line was calculated using a modified four parameter model of coupled oscillators [12]. The diagram was numerically analysed using the following equation:

$$\varepsilon(\omega) = \varepsilon_{\infty} \frac{\prod_{j=1}^2 (\omega^2 + i\gamma_{Lj}\omega - \omega_{Lj}^2)}{\omega(\omega + i\gamma_p)(\omega^2 + i\gamma_T\omega - \omega_T^2)} \prod_{n=1}^p \frac{(\omega^2 + i\gamma_{Lon}\omega - \omega_{Lon}^2)}{(\omega^2 + i\gamma_{Ton}\omega - \omega_{Ton}^2)} \prod_{k=1}^3 \frac{(\omega^2 + i\gamma_{Lok}\omega - \omega_{Lok}^2)}{(\omega^2 + i\gamma_{Tok}\omega - \omega_{Tok}^2)} \quad (1)$$

where  $\omega_{Lj}$  and  $\gamma_{Lj}$  parameters of the first numerator represented the eigen frequencies and the damping factors of the longitudinal plasmon – phonon waves (LF+LO), respectively;  $\omega_T$  and  $\gamma_T$  are the frequency and damping factor of the transverse phonon mode;  $\gamma_p$  is the damping factor of plasmon and  $\varepsilon_{\infty}$  is the high frequency dielectric permittivity. The second term in eq. 1 represents the Ce impurity local modes. The  $\omega_{Lok}$  and  $\omega_{Tok}$  are the longitudinal and transverse frequencies and  $\gamma_{Lok}$  and  $\gamma_{Tok}$  stand for the damping factors of uncoupled modes of the host crystal.

In the fitting procedure we determined the transverse phonon frequency (at about 34 cm<sup>-1</sup>) [13] then an oscillator of a weak intensity, at about 84 cm<sup>-1</sup>, which is a mode from the edge of the Brillouin zone. Then we obtained a longitudinal mode of PbTe at about 105 cm<sup>-1</sup>, which is in agreement with the values found in literature [13]. Dielectric permittivity was calculated to be about 23. The plasma frequency  $\omega_p$  was also determined as described in lit. [12]. It was about 180 cm<sup>-1</sup>.

We also determined two local modes of cerium at about 228 cm<sup>-1</sup> and 373 cm<sup>-1</sup>. The local modes of cerium could belong to one of three electron states: Ce<sup>+</sup>, Ce<sup>2+</sup> or Ce<sup>3+</sup>. The two electron state of cerium Ce<sup>+</sup> is a more stable state than the metastable single electron state Ce<sup>2+</sup> or the empty state Ce<sup>3+</sup>. We suppose that cerium behaves similarly to elements of the IIIA group previously explained, when PbTe was doped either with In or B [14, 15]. That means that the metastable Ce<sup>2+</sup> state may transfer to more stable forms as follows:



The electron from the Ce<sup>+</sup> state may transfer to the conduction band as follows:



The position of the pinned Fermi level depends on the balance between Ce<sup>+</sup> and Ce<sup>3+</sup> impurity states. When these two electron local states are equal then the Fermi level is pinned near the top of the valance band and the sample is of the *p*-type.

It is interesting to notice that the free carrier concentration of lead telluride doped with cerium increased from 1.1×10<sup>18</sup> to 3.1×10<sup>18</sup> cm<sup>-3</sup>, when the temperature of the sample was decreased from room to liquid nitrogen temperature.

### 4. Conclusion

In this work we have shown the far infrared reflectivity spectrum of cerium doped lead telluride single crystals at room temperature.

A strong plasmon – LO phonon interaction was observed as well as two local vibrational cerium impurity modes. We feel that the observed cerium modes belong to the stable Ce<sup>+</sup> and Ce<sup>3+</sup> charge states of impurity, which approaches in energy the valance band edge and the Fermi level was pinned by the one electron local state Ce<sup>2+</sup> which is linked to the valance band top.

## References

- [1] P. M. Nikolić, *Britt. J. Appl. Phys.*, **16**, 1075(1965).
- [2] P. M. Nikolić, *Britt. J. Appl. Phys.*, **18**, 897(1967).
- [3] A. J. Strauss, *Trans. Met. Soc. AIME*, **242**, 355(1967).
- [4] B. A. Akimov, V. P. Zlomanov, L. I. Ryabova, S. M. Chudinov, O. B. Yatsenko, *Fiz. Tech. Poluprovod.*, **13**, 1239(1979)/ *Sov. Phys. Semicon.* **13**, 759(1979).
- [5] B. A. Akimov, N. B. Brandt, L. I. Ryabova, D. R. Khokhlov, S. M. Chudinov, O. B. Yatsenko, *Sov. Phys. JETR Lett.*, **31**, 273(1980).
- [6] B. A. Akimov, A. V. Dmitriev, D. R. Khokhlov, L. I. Ryabova, *phys. stat. sol. (a)*, **137**, 9(1993).
- [7] V. I. Kaidanov, R. B. Melnik, I. A. Chernik, *Sov. Phys. Semicon.*, **7**, 522(1973).
- [8] B. A. Akimov, N. B. Brandt, K. R. Kurbanov, L. I. Ryabova, A. T. Khasanov, D. R. Khokhlov, *Sov. Phys. Semicon.*, **17**, 1021(1983).
- [9] I. I. Ivanchik, D. R. Khokhlov, A. I. Belogorokhov, Z. Popović, N. Romčević, *Semiconductors*, **32**, 608(1983).
- [10] E. P. Skipetrov, N. A. Chernova, E. I. Slgn'ko, Yn. K. Vygranenko, *phys. stat. sol. (b)*, (1998).
- [11] I. I. Ivanchik, D. R. Khokhlov, S. V. Ponomarev, A. A. Terekhov, E. I. Slgh'ko, Yn. K. Vugranenko, *A. de Visser, Priv. Comm.*
- [12] A. A. Kukharski, *Sol. Stat. Comm.*, **13**, 1761(1973).
- [13] Yul. Ravich, B. A. Efimova, T. A. Smirnov, *Semiconducting Lead Chalcogenide*, Ed. L. S. Stil'bans, Plenum Press, New York (1970).
- [14] B. M. Vul, I. D. Voronova, G. A. Kalyuzhnaya, T. S. Mamedov, T. R. Ragimova, *Sov. Phys. JETR Lett.*, **18**, 29(1971).
- [15] P. M. Nikolić, N. Romčević, K. Radulović, S. S. Vujatović, S. Đurić, V. Blagojević, P. Mihajlović, D. Siapkas, T. T. Zorba, *Sci. Sinter.*, **31(2)** 125(1999).