OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 5, May 2010, p. 668 - 670

Optical far infrared properties of $PtSb_2$

N. NIKOLIĆ, S. S. VUJATOVIĆ[a], T. IVETIĆ[a], K. M. PARASKEVOPOULOS[b], T. T. ZORBA[b], O. S. ALEKSIĆ, V. BLAGOJEVIĆ[c], M. V. NIKOLIĆ, P. M. NIKOLIĆ[a*]
Institute for Multidisciplinary Research, Kneza Višeslava 1, 11000 Belgrade, Serbia
[a]Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihailova 35/IV, 11000 Belgrade, Serbia
[b]Physics Department, Solid State Section, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[c]Faculty of Electrical Engineering, University of Belgrade, Bulevar Kralja Aleksandra 73, 11000 Belgrade, Serbia

Far infrared reflection spectra measured at room temperature were used to investigate vibrational properties of $PtSb_2$ single crystals. The experimental results were analyzed using a dielectric function taking into account the existence of plasmon-ionised impurity-phonon interactions. Together with strong coupling three infrared active lattice modes at about 143, 187 and 202 cm^{-1} were observed. These results were discussed with respect to calculated literature vibrational frequencies. Electrical properties of single crystal $PtSb_2$ were also measured at room temperature.

(Received May 12, 2010; accepted May 20, 2010)

Keywords: Pnictides, Far infrared reflectivity

1. Introduction

Vibrational spectroscopy on solids is an interesting method for bonding characterization of solids with covalent substructures. Recently, it was studied in detail for pyrite type pnictides ME_2 (M = metal, E = pnicogen) [1]. Geometrical and vibrational properties of the following pyrite-type pnictides: SiP_2, PtN_2, PtP_2 and $PtAs_2$ were studied at LDA (local density approximation) level and this method provided excellent agreement with experimental work. In short, the calculated frequencies of these compounds were summarized and then compared to the available IR and Raman data.

It is interesting to notice that although $PtSb_2$ belongs to the series of platinum pnictides PtE_2 (with E = P, As, Sb, Bi) it was not included in the mentioned work although it has got the same pyrite structure and its semiconducting properties were considered a long time ago [2, 3]. In [2] electrical, magnetic and some optical properties of $PtSb_2$ over a wide temperature range: 78 K – 120 K were considered. The room temperature energy gap is rather low – about 0.07 eV, and that is very small for this material with a rather high melting temperature (1226°C). Atomistic simulation studies of FeS_2, $PtSb_2$ and $PtAs_2$ using derived interatomic potentials were recently calculated and compared with experimental results [3]. More recently [4] far infrared reflection spectra of hot-pressed samples of these pyrites were presented in the range from 40 – 700 cm^{-1}. In this work we measured FIR properties of single crystal $PtSb_2$ samples and performed numerical analysis of the experimental data.

2. Experimental and discussion

A single crystal $PtSb_2$ ingot was prepared using the standard Bridgman method [5]. High purity elements (6N) were used as the source material. Samples were cut from the ingot and then highly polished before they were used for measurements. Far infrared reflectivity spectrum of a PtSb2 sample was measured at room temperature using a Bruker IFS-113V spectrometer and it is given in Fig. 1. The plasma minimum for this sample was observed at about 450 cm^{-1}. At lower frequencies three small minima were observed at about 200 cm^{-1}, 184 cm^{-1} and about 140 cm^{-1}.

Table 1. Optical parameters of phonon and plasmons obtained by oscillator fitting of $PtSb_2$.

ω_p	γ_p	ε_∞	ω_{01}	γ_{01}	ω_{02}	γ_{02}	ω_{03}	γ_{03}	ω_{04}	γ_{04}
444.6	176	32.4	143	5	187	7.4	202	8.9	499	75507

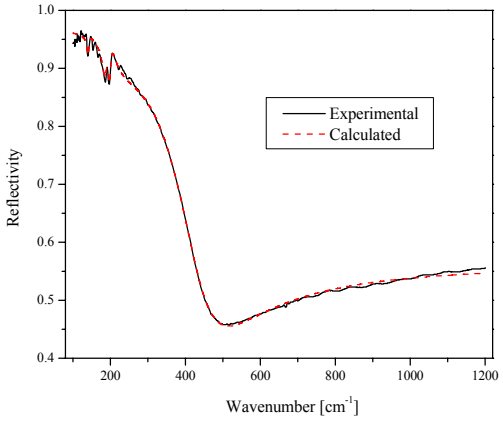

Fig. 1. Measured (solid line) and calculated (dash) infrared reflectivity spectra of $PtSb_2$.

The experimental results were numerically analyzed using a modified four-parameter model for the dielectric function [6] 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 [7]. Details of this modified model are given in our previous work [8]. The values of the calculated optical parameters are given in Table 1 where the plasma frequency is given with ω_p; its damping factor is denoted with γ_p and ε_∞ is the high frequency dielectric permittivity calculated as:

$$\varepsilon_\infty = \left[\frac{1+\sqrt{R_\infty}}{1-\sqrt{R_\infty}}\right]^2,$$

where R_∞ is the experimental value of the reflectivity coefficient at the upper limit of the wave number measured interval. For the fitting procedure the starting values of all parameters were previously determined using Kramers-Krönig analysis [9]. Transversal (TO) optical modes (ω_{01}, ω_{02}…) and their damping factors (γ_{01}, γ_{02}…) are also given in Table 1. All values are given in cm^{-1}, except ε_∞.

Since $PtSb_2$ has a pyrite structure, one can calculate the number of active IR modes, and compare it with our experimental data. Group theory analysis enabled determination of the number of modes for the Pa3 pyrite structure with formula units per unit cell as:

$$\Gamma = A_g + 2Au + E_g + 2E_u + 3F_g + 6F_u, \quad (1)$$

where A_g, E_g and F_g represents Raman active ($\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$), ($\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}$) and ($\alpha_{xx}$, α_{xz}, α_{yz}) modes, ($2A_u + 2E_u$) are "silent" modes, F_u characterizes the five IR active and one acoustic mode.

Looking at Fig. 1 it is obvious that three IR modes can clearly be seen at about 141, 187 and 203 cm^{-1} and the plasma frequency can be noted at about 450 cm^{-1}. Lutz [4] observed all five modes, which are theoretically predicted, but in plasma free spectra on hot pressed pellets.

The positions of the optical modes observed for our single crystal $PtSb_2$ sample were, we believe, more accurately obtained. We also calculated the imaginary part of the complex dielectric function, the response function and the absorption coefficient versus wavenumbers, respectively for our single crystal $PtSb_2$ sample; these diagrams are given in Figs. 2, 3 and 4, respectively. All FIR and IR observed modes could be also compared with DFT (density functional theory calculations) [1]. Other pyrite-type pnictides have been studied at LDA (local density approximation) using the Crystal06 code (e.g. [1]). One can see that the results for IR modes given for PtN_2, PtP_2 and $PtAs_2$ are the IR modes we observed for $PtSb_2$ in the same IR range. So the obtained vibrational data in this work for $PtSb_2$ could be quite interesting for further studies of these isostructural compounds.

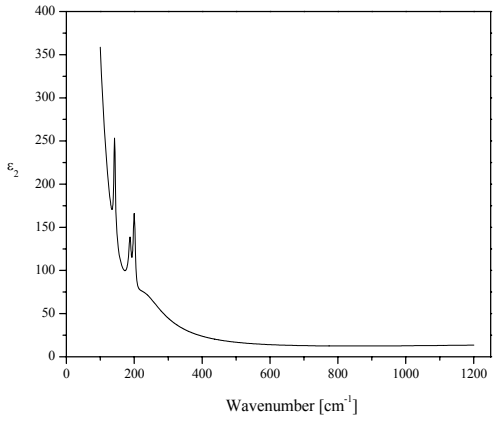

Fig. 2. Imaginary part of the complex dielectric function vs. wavenumber of $PtSb_2$.

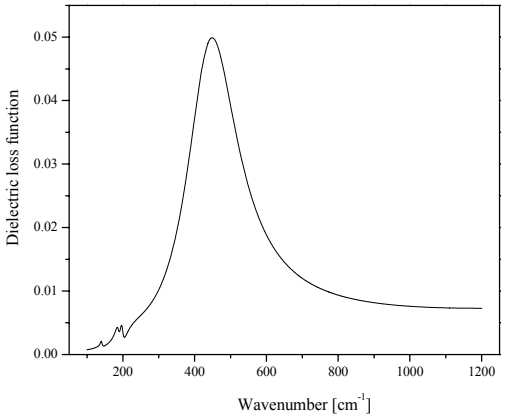

Fig. 3. Response function vs. wavenumber calculated for $PtSb_2$.

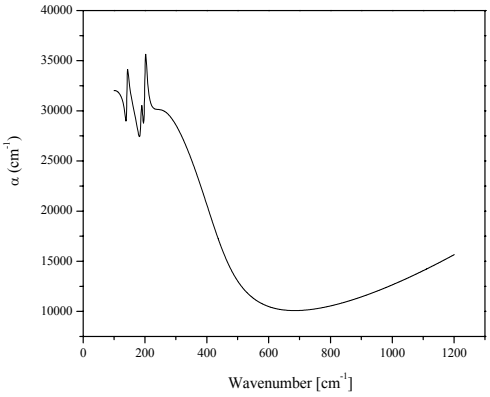

Fig. 4. Absorption coefficient vs. wavenumber calculated for $PtSb_2$.

We also measured the Hall coefficient, conductivity and Hall mobility of our $PtSb_2$ sample, and the following data were obtained: conductivity-σ (1/Ωcm) 341; mobility-μ (cm^2/Vs) 237 and free carrier concentration $p \cong 9 \cdot 10^{18}$ [cm^{-3}]. These data show that our sample is of reasonable quality compared with literature known data [2].

3. Conclusions

In this work the room far infrared spectra of single crystal $PtSb_2$ have been measured and analyzed. We observed a strong plasmom-LO phonon interaction and also three free carrier contributions due to the deviation from stoichiometry. The fourth mode was registered also, but it was very week. The fifth mode whose existence was theoretically determined using group theory analysis is expected to be at a rather low frequency judging by literature experimental data [4] for hot pressed $PtSb_2$ samples.

Acknowledgements

This research was performed within the project "Investigations of Corelations in Triad Synthesis-Structure-Properties for Functional Materials", No. 142011G financed by the Ministry for Science and Technological Development of the Republic of Serbia.

References

[1] M. Meier, R. Weihrich, Chem. Phys. Lett. **461**, 38 (2008).
[2] D. H. Damon, R. C. Miller, A. Sager, Phys. Rev. **138,** A636 (1965).
[3] P. E. Ngoepe, P. S. Ntoahae, S. S. Mangwejane, H. M. Sithole, S. C. Parker, K. V. Wright, N. H. de Leeuw S. Afr. J. Sci. **101,** 480 (2005).
[4] H. D. Lutz, G. Schneider, G. Kliche J. Phys. Chem. Solids **46,** 437 (1985).
[5] B. A. Akimov, A. V. Nikorich, L. I. Ryabova, N. A. Shirokova, Fiz. Tekh. Poluprovodn **23,** 1019 (1989).
[6] F. Gervais, B. Piriou, Phys. Rev. B **10,** 1642 (1974).
[7] A. A. Kukharskii, Solid State Commun. **13,** 1761 (1973).
[8] P. M. Nikolić, W. König, S. S. Vujatović, V. V. Blagojević, D. Luković, S. Savić, K. Radulović, D. Urošević, M. V. Nikolić, J. Alloys Compd. **433,** 292 (2007).
[9] D. M. Roessler, Br. J. Appl. Phys. **16,** 1119 (1965).
[10] H. Vogt, T. Chattopadhyay, H. J. Stolz, J. Phys. Chem. Solids **44,** 869 (1983).

*Corresponding author: pantelija.nikolic@sanu.ac.rs