Science of Sintering, **39** (2007) 223-228

doi: 10.2298/SOS0703223N

UDK 662.785:661.852

Far Infrared Properties of Sintered PbTe Doped with Boron

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Abstract:

Far infrared spectra of sintered PbTe doped with boron were analyzed. The measured infrared spectra were fitted using a modified plasmon-phonnon interaction model with two additional oscillators (at about 195 cm^{-1} and 285 cm^{-1}) representing local B-impurity modes. The obtained results were compared with previously published data for a single crystal PbTe sample doped with boron.

Keywords: *PbTe, Boron, Sintering, Infrared Reflectivity.*

Introduction

Properties of $A^{IV}B^{VI}$ compounds and alloys doped with group III elements (In, Ga, Tl, B) have been intensively studied for more than one decade [1-5]. Special attention has been paid to doped alloys, where impurity centers provide the existence of Fermi level pinning and the persistent photoconductivity effect at low temperatures [2]. Although particular attention has been paid to alloys doped with indium, the strongest effect was noticed when PbTe was doped with boron, because the boron atom is very small compared to the Pb and Te atoms. Boron ions in PbTe are not at the center of inversion symmetry and vibrational local modes could be both far infrared and Raman active [4,5]. For a boron concentration of about 3 at%, the plasma frequency was the lowest at about 130 cm^{-1} [4]. As a consequence of this one should expect a decrease of the free carrier concentration and increased mobility. These properties are important for the production of infrared high performance lasers and lead telluride-based sensors for space-born applications. Since all these properties were determined for single crystal samples whose production is expensive the idea was to determine if sintered PbTe+B samples would have similar properties. Such sintered samples could be used for making much cheaper thick film devices. Thus, in this

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work we have studied sintered (from powder) lead telluride samples doped with boron. Their structural and optical far-infrared properties were measured and compared with single crystal samples [4,6].

Experimental

PbTe powder (Alfa, purity 6N) was milled with 3 at % B (Alfa, purity 2N) and then pressed into pellets 10mm in diameter with a pressure of 1.5 GPa. The pellets were then evacuated in quartz tubes and sintered at 600 and 700°C for 10 hours (denoted S1 and S2, respectively). These two sintering temperatures were chosen in order to get some idea of the influence of the sintering temperature knowing that the melting temperature of PbTe is 917°C. The sintering time of 10 hours was selected as a time for which the sample should be fully sintered. Obviously, in order to determine the optimal sintering procedure, a study of the influence of different sintering times and temperatures should be conducted. In this work we wanted to analyze whether sintering PbTe with Boron gave samples with applicable properties.

The crystal structure of the samples obtained was investigated using X ray diffraction on a Philips PW 1710 difractometer with Ni-filtered CuK_α radiation. SEM analysis was performed using a JEOL LSM-840A scanning electron microscope. Room temperature far infrared reflectivity measurements were performed with near normal incidence light in the range between 50 and 500cm^{-1} using a Bruker 113V FTIR spectrometer. All samples were polished first with silicon carbide P1500 sandpaper and then with 3μm grade diamond paste.

Results and discussion

X-ray diffractograms obtained for samples S1 and S2 are given in Fig. 1. All Bragg reflections belong to a PbTe lattice with a NaCl space group.

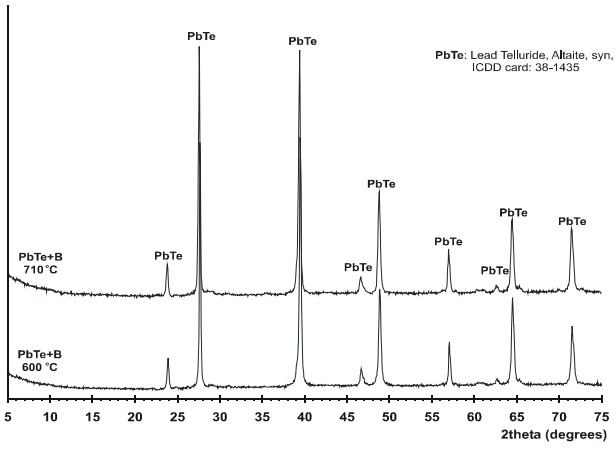

Fig. 1 X-ray diffractograms of sintered PbTe doped with Boron

The microstructure of sample S1 seen on Fig. 2a is composed of bigger and smaller grains with scattered regions where open porosity is displayed. At 700°C (Fig. 2b) – sample S2 the structure becomes more homogeneous, compared to the microstructure seen on Fig. 2a,

with obvious formation of areas with closed porosity indicating the final stage of sintering process.

The density measured for these two samples was 6.084 g/cm^3 for sample S1 and 6.464 g/cm^3 for sample S2. The density of single crystal PbTe is 8.24 [7]. Thus the density measured for the sintered samples was 73.8% and 78.8% of the single crystal value, showing that the obtained sintered samples had a certain porosity that was confirmed by microstructure analysis (fig. 2). There is obviously space for improvement of the sintering conditions (time and temperature) applied in order to achieve higher density values.

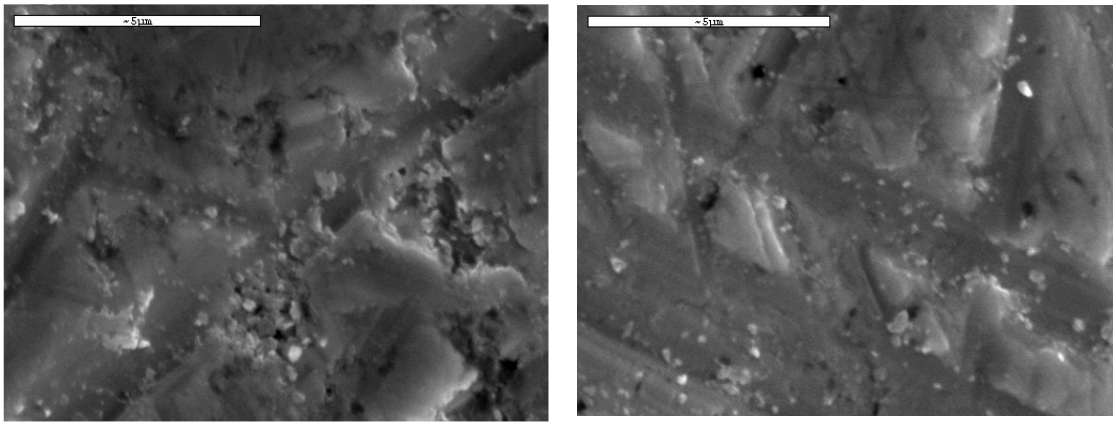

Fig. 2 Micrographs of PbTe doped with Boron sintered at 600^{o}C (a) and 700^{o}C (b

The room temperature reflectivity diagram, as a function of the wave number, for sample S1 is given in Fig. 3a and for S2 in Fig. 3b. Experimental results are given with circles, while the full line was calculated using a modified four parameter model for the dielectric function [8] that takes into account the existence of plasmon-LO phonon interactions [9]:

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

where ω_{lj} and γ_{lj} are parameters of the first numerator which represent the eigenfrequencies and damping factors of the longitudinal-phonon (LP+LO) waves, which arise as a result of interactions of the initial (ω_{LO}, PbTe and ω_p) modes. First denominator parameters correspond to transversal (TO) vibrations, γ_p is the damping factor of plasma. The second term in equation (1) represents the local impurity modes. The third term represents uncoupled modes of the host crystal. The reflectivity spectra were measured down to 50 cm^{-1}, so the value at 32 cm^{-1} for the transverse phonon frequency, ω_t, was taken from the literature. [3]. The values of plasma frequency were calculated using the following equation [9]:

$$\omega_p = \frac{\omega_{l1}\omega_{l2}}{\omega_t} \quad (2)$$

The values of the optical parameters calculated using equations 1 and 2 are given for both samples in Tab. I.

Tab. I Optical parameters determined for sintered PbTe doped with Boron (all values are given in cm^{-1}, except μ_p that is in cm^2/Vs and ε_∞)

	ω_{l1}	γ_{l1}	ω_{l2}	ω_{L1}	γ_{L1}	ω_{01}	γ_{01}	ω_{02}	γ_{02}	ω_{LOPbTe}	γ_{LOPbTe}	ω_p	ε_∞	μ_p
S1	126	31.2	30.8	249	147	196	90	286	103	104	807	121	13.3	980
S2	134	49	30.8	249	90	196.8	70	285	75	104	316	132	17.6	1193

Looking at Fig. 3, one can see that besides well exposed plasma, there are two local modes better exposed for the sample sintered at higher temperature (700°C). Also in agreement with this statement one can see in Tab. I that the damping factors of both modes decrease for the sample sintered at the higher sintering temperature. The plasma frequencies are slightly different. Using the method of Moss et al [10] we calculated the optical mobility of free carriers in both samples. For sample S1 the optical mobility was calculated to be 980 cm^2/Vs while for the sample S2 it was 1193 cm^2/Vs. Looking at the shape of plasma minima for both samples in Fig. 3, this is expected.

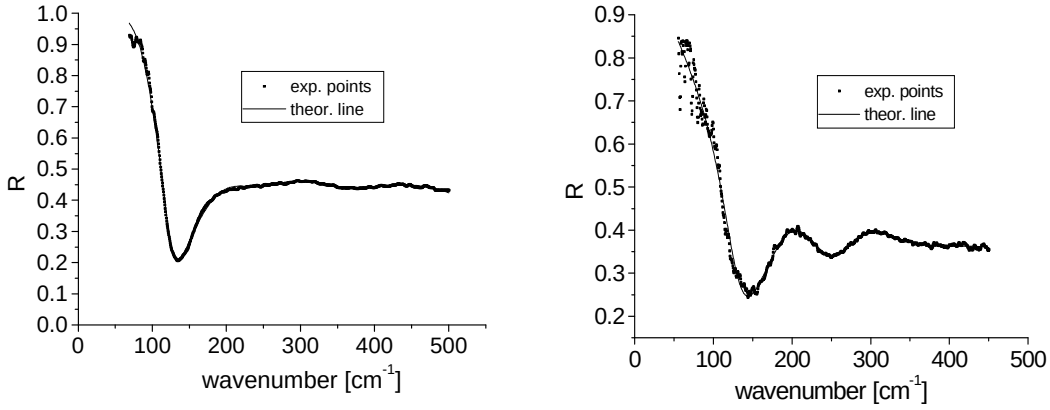

Fig. 3 Measured (circles) and calculated (full line) far infrared reflectivity spectra of PbTe doped with Boron sintered at 600°C (a) and 700°C (b)

Using the hot point method, we concluded that both our sample were of the "p" type. Knowing that the standard value for room temperature hole mobility of PbTe is only 750 cm^2/Vs one can say that our sintered PbTe doped with boron samples are of a very good quality. This means that these sintered samples could be used for making IC detectors and sensors for infrared astronomy. Our results can be compared only with several published papers [4,5].

For single crystals PbTe doped with boron, three local modes at 156 cm^{-1}, 210 cm^{-1} and 260 cm^{-1} were observed and analyzed [4]. There it was supposed that, similarly to PbTe doped with In, boron in PbTe has an unstable B^{+2} state which may transfer to a less unstable form: $2\ B^{+2}=B^{+}+B^{3+}$. Also, the B^+ state can transfer as follows: $B^+ = B^{3+}+2e$. The metastable state (B^{+2}) for single crystal PbTe doped with boron was determined at 156cm^{-1} while two electron stable states (B^+) were at about 210 cm^{-1} and finally the (B^{3+}) empty center was at about 260 cm^{-1} [4]. In the case of sintered PbTe doped with boron samples only two impurity modes can be registered, one at about 195 cm^{-1} instead of 210 cm^{-1} and the second one at about 285 cm^{-1} instead of at 260 cm^{-1}. This mode shift could be the consequence of the applied sintering procedure. Compared to single crystal samples the sintered samples have a lower

density, resulting in open and closed porosity that is clearly seen in the sample microstructures (Fig. 2). Porous PbTe was studied in [11] and the spectral dependences found differed for the ones obtained for the single crystal. This was attributed to possible quantum size effects [11,12] and this could also be the case for sintered PbTe with Boron. The third local mode registered at about 156 cm^{-1} for single crystal [4] could not be observed for our sintered samples as we observed a plasma effect in that frequency range that was much stronger and could cover any other effect (mode).

Conclusion

In this work we have measured and analyzed far infrared reflectivity spectra of PbTe samples doped with 3at% Boron sintered at two temperatures (600 and 700^{o}C, for 10 h). We observed plasma minima for both samples, sintered at 600°C and 700°C, at very low wave numbers that is consequence of the high sample quality. This was proved by calculations of the optical mobility of free carriers for both samples that was higher than for standard single crystal pure PbTe. This means that sintered PbTe doped with boron has improved properties and could be used for making much cheaper thick film sintered sensors than single crystal ones. Two local impurity Boron modes were observed at about 195cm^{-1} and 285 cm^{-1} and their position slightly differs from single crystal modes due to the applied sintering procedure or even possible quantum size effects.

Acknowledgement

This work was performed as part of projects 6150B and 142011G financed by the Ministry for Science of the Republic of Serbia. The authors are grateful to the Greek Secretariat of Research and Development for partial support under the bilateral program between Serbia and Greece.

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Садржај: *Анализирани су инфрацрвени спектри олово телурида допираног са бором. Измерени спектри су фитовани коришћењем модела плазмон-фононске интеракције са два додатна осцилатора (на око 195 и 285 cm^{-1}) који представљају локалне модове бор нечистоће. Добијени резултати су упоређени са раније публикованим подацима за кристал олово телурида допираног бором.*

Кључне речи*: Олово телурид, Бор, синтеровање, инфрацрвена рефлексија*