Inelastic X-Ray Scattering Studies of Phonon Dispersion in PbTe and (Pb,Cd)Te Solid Solution

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PbTe and its solid solution (Pb,Cd)Te containing 2% of CdTe and PbTe grown by self-selecting vapour growth technique were investigated by inelastic X-ray scattering using synchrotron radiation. The ID28 beamline at ESRF with the incident photon energy of 17794 eV and the energy resolution of 3 meV was applied for that purpose. The measurements were performed at room temperature along [001]-type high symmetry direction in the Brillouin zone. In spite of a very low energy of phonon branches they can be determined by inelastic X-ray scattering with a high accuracy. The transversal acoustic phonon dispersion obtained by inelastic X-ray scattering corresponds well to those resulting from inelastic neutron scattering measurements and *ab initio* calculations. Apart from expected structures corresponding to the bulk phonons an additional scattering related to the crystal surface properties was observed in the inelastic X-ray scattering spectra. The analysis performed with the use of secondary ion mass spectroscopy technique demonstrated a presence of a thin oxide layer at sample surfaces.

1. Introduction

The study of atomic dynamics in solids at energies, E, and momentum transfer, Q, characteristic of collective motions is traditionally the domain of neutron spectroscopy. The inelastic neutron scattering (INS) developed for the last sixty years is now well established experimental technique, usually applied for a determination of phonon dispersion in crystals. In the case of the INS experiment a typical required volume of single crystal should be a substantial part of 1 cm^3. However, there exists another experimental tool, which can be very useful for studies of the phonon dispersion, which does not require a big samples size. The inelastic X-ray scattering (IXS) method, developed since the pioneering experiments in 1987 [1] starts to be standard experimental technique applied to study the lattice dynamics in selected semiconductors which do not meet typical requirements of the INS method: small size single crystals and thin layers or compounds containing elements (e.g. B) which strongly absorb neutrons. The IXS technique due to small linear beam size (down to ≈30 μm) allows to study even slight quantities of given material but because of a requirement of extremely high energy resolution (at least $\Delta E/E = 10^{-7}$) was mostly applied in the past for studies of phonons with high energy in selected semiconductors composed of relatively light elements.

Among the semiconducting compounds attracting a lot of attention in the recent years are crystals which exhibit thermoelectric properties. Thermoelectric materials are of great interest for both the basic physics and the energetic applications because they can transform heat into electricity. The thermoelectric figure of merit $ZT = \sigma^2 T/\kappa$ determines the maximum efficiency of the conversion process, where σ denotes the electrical conductivity, S — the Seebeck coefficient, T — the temperature, and κ — the heat conductivity. The materials with structural defects and micro/nanostructural features that hinder the propagation of phonons while preserving σ are highly desired for thermoelectric applications because atomic vibrations carry most of the heat in semiconductors and the lattice contribution to the heat transport can be as high as ≈90%. However, the difficulty of fabricating materials with such tailored nanostructures and their thermodynamic stability at required temperature is still big challenge for the scientists. Investigation and interpretation of the lattice dynamics is essential in order to understand the heat and the electron transport in a semiconductor.

Lead telluride (PbTe) is well known thermoelectric semiconductor with narrow energy band gap and the rock salt (RS) crystal structure. The lattice dynamics of this compound was determined long time ago by the INS technique [2]. Recently, the previously unknown details of PbTe lattice dynamics and proposed new physical mechanisms responsible for its high thermoelectric efficiency attracted a lot of attention [3]. On the other

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hand, a modification of the heat transport in this material by high doping or mixing/alloying with a variety of compounds seems to be a hot topic for the last few years. The search for mechanically stable PbTe-based thermoelectric materials by the crystal doping with Sn, I, or Na [4], improved mechanical properties of PbTe containing Ge [5], Na [6] and Ca [7] are just a few examples of papers related to the problem mentioned above. In particular, the properties of (Pb,Cd)Te solid solution formed by PbTe alloying with CdTe — well-known and widely investigated compound of II–VI type — were the subject of several reports in the past. However, CdTe is a semiconductor crystallizing in the zinc blende structure and the difference in PbTe and CdTe crystal symmetry for many years was a reason for serious difficulties in a growth of (Pb,Cd)Te solid solution. Recent successful growth of big, metastable (Pb,Cd)Te crystals with the RS structure by self-selecting vapour growth (SSVG) method in the Institute of Physics PAS changed this situation [8–11]. Due to the application of SSVG technique solid solution containing up to 12% of CdTe can be obtained in the form of single crystals with the volume exceeding 1 cm^3. Several such crystals were recently investigated by us using the INS technique in order to verify, e.g., some findings reported in Ref. [3], selected preliminary results of these studies can be found in Ref. [12]. In the meantime we decided to check if the IXS technique is suitable also for the accurate determination of the low-frequency phonon dispersion, observed in compounds composed of heavy elements. The goal of the present work was to determine the dispersion of a few selected phonon branches in PbTe and (Pb,Cd)Te and to compare it with our previous results obtained by the INS technique and present *ab initio* study.

2. Experimental and calculation details

The single crystals of (Pb,Cd)Te solid solution containing 2% of CdTe as well as pure PbTe were grown by SSVG method at the Institute of Physics PAS [8–11]. The structure quality of samples and the chemical composition of the (Pb,Cd)Te solid solution were determined by X-ray powder diffraction utilizing X'Pert Philips (PANalytical) diffractometer and the Cu K_{α_1} radiation. The structure of single crystals was checked by neutron diffraction using G4-3 neutron spectrometer installed on the cold neutron source at Laboratoire Léon Brillouin in France. The same spectrometer served for the INS measurements at room temperature, the initial neutron momentum fixed at $k_i = 2.2$ Å^{-1} and the energy resolution of 0.5 meV were applied for this purpose. The IXS investigations with the use of synchrotron radiation were performed at ESRF on the ID28 beamline with the incident photon energy of 17794 eV and the energy resolution of 3 meV. The measurements were performed at room temperature along [001]-type high symmetry direction in the Brillouin zone.

The chemical composition of the surface of investigated crystals was determined by the secondary ion mass spectroscopy (SIMS) measurements using a TOF-SIMS V instrument. TOF-SIMS depth profiles were measured with the instrument working in the dual-beam mode. The sputtering was performed using the 1 keV (15 nA) Cs$^+$ ion beam, rastered over the area of 300×300 µm^2. The area of analysis was in the middle of the sputtering crater using 30 keV (1.3 nA) Bi$^+$ primary ion beam, rastered over the area of 100×100 µm^2.

The PbTe phonon dispersion was modelled by first-principles calculations based on density functional theory (DFT) and the force constants direct method [13]. This procedure was successfully adopted in the past for broad variety of compounds, including unstable structures [14], semiconductors with small phonons dispersions [15] or very low acoustic phonons frequencies [16] as well as minerals with wide phonon spectrum and local modes [17]. In present calculations the Blöchl full potential projector augmented-wave (PAW) method within the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form has been employed. The Brillouin-zone integration has been carried out with a $4 \times 4 \times 4$ k-point mesh generated with the Monkhorst–Pack scheme. The plane-wave basis set was limited by a kinetic energy cutoff at 240 eV. For structural and phonon calculations we have used the $2 \times 2 \times 2$ supercell containing 64 atoms (for further details see Ref. [17] and papers cited there).

3. Results and discussion

Single bulk crystal PbTe and (Pb,Cd)Te solid solution with 2% of CdTe was used to investigate phonon dispersion along [001]-type direction. Apart from two well pronounced structures corresponding to an absorption and an emission of the longitudinal acoustic phonon mode the wide, much less intense structure is seen in Fig. 1 in the central part of the spectrum. Due to a supposition that this structure is caused by an additional X-ray scattering resulting from a presence of thin layer at sample surfaces, the supplementary measurements with the use
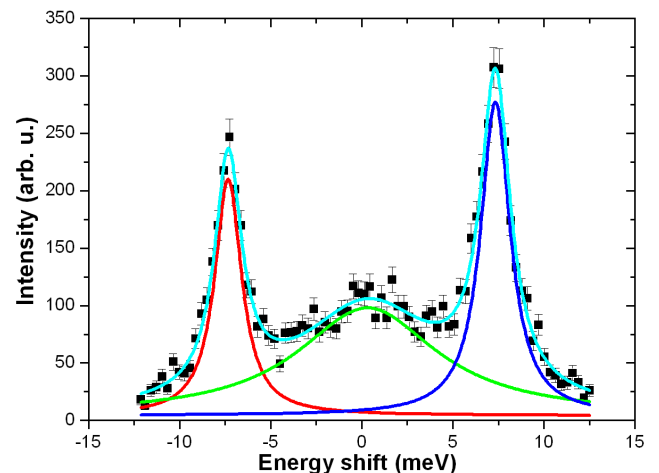

Fig. 1. Typical room temperature IXS spectrum taken for PbTe along [001]-type direction in the middle of the Brillouin zone. The solid curves illustrate the best fit to experimental points (details in the main text).
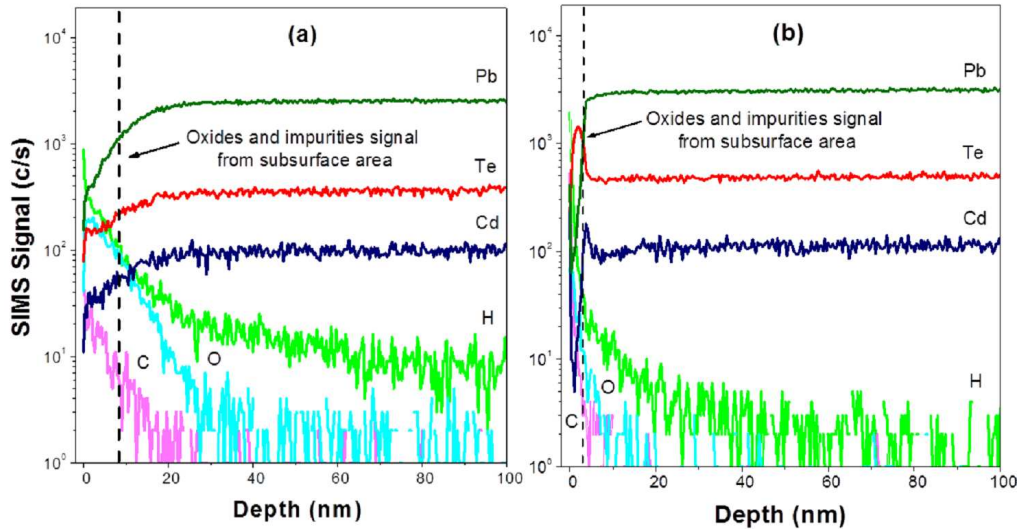
Fig. 2. (a) SIMS depth profiles for (Pb,Cd)Te containing 2% of CdTe before the etching, (b) SIMS depth profiles after the etching for the same sample.

of the SIMS technique were performed at University of Rzeszów. The SIMS spectra were collected both for as-grown samples and for the samples after etching which should remove this layer if it exists. The results of measurements before and after etching are shown in Fig. 2a and b, respectively. The analysis of experimental data demonstrated a presence of a thin, probably less than 10 nm thick "pollution" layer at the surface of as-grown crystals. This layer is composed of oxides (probably tellurium oxide, H and C) and can be removed by etching (see Fig. 2b). The next IXS experiment with the use of the same crystals after etching is under preparation now, it should definitely confirm the origin of an additional structure in the IXS spectra.

The transversal acoustic (TA) phonon dispersion determined along [001]-type direction by the IXS and INS experimental techniques is compared with the theoretical predictions resulting from DFT calculations in Fig. 3. A perfect agreement of experimental data resulting from both methods above mentioned is seen, these data are also very well described by the theory. The results presented in Fig. 3 confirm an applicability of the IXS technique for precise studies of lattice excitations also in materials composed of heavy elements and thus exhibiting very low energy of relevant phonons.

4. Conclusions

The selected phonon dispersion determined by the IXS measurements confirmed within an experimental error our INS data and accurate first-principles calculations, demonstrating a high efficiency of the IXS technique for studies of low-frequency excitations. Comparison of the SIMS depth profiles before and after etching shows the presence of oxide layer and some impurities (H, C) at surfaces of investigated samples during IXS measurements.
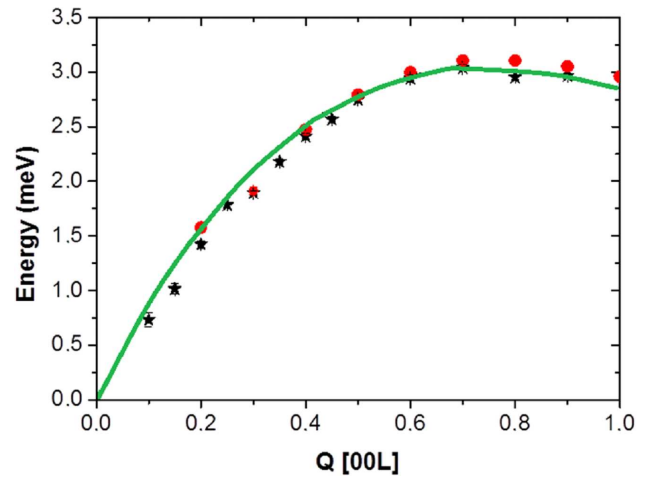

Fig. 3. Comparison of the TA phonon mode dispersion along [001]-type high symmetry direction in PbTe determined at the present work by IXS (asterisk) and INS measurements (circles). The solid line corresponds to theoretical prediction of the TA dispersion resulting from the *ab initio* calculations.

The presence of surface layer mentioned above caused an extra X-ray scattering resulting in an additional structure of accumulated IXS spectra.

Acknowledgments

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