

Pb_{1-x}Mn_xTe and PbTe_{1-x}S_x compounds and their optical properties

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Abstract: Pb_{1-x}Mn_xTe crystals were obtained by the Bridgman method and PbTe_{1-x}S_x crystals were grown by the vapour–liquid–solid technique. The structural properties of Pb_{1-x}Mn_xTe ($x \leq 0.10$) and PbTe_{1-x}S_x ($x \leq 0.05$) were observed by X-ray powder diffraction analysis. The optical properties were studied by Raman spectroscopy as a function of temperature. Measurements on these samples of different composition gave information about the Mn and S position in the lattice (off-centering), their clustering and ordering, as well as of the influence of these processes on the crystal structure and properties. The model of phonon behaviour based on the Random Element Isodisplacement model was applied, and it was found that the phonons in PbTe_{1-x}S_x show a two-mode behaviour (each TO-LO mode pair of the end members degenerates to an impurity mode), while the Pb_{1-x}Mn_xTe optical phonons have a intermediate one-two-mode behaviour (the LO-mode frequency shifts continuously from PbTe to MnTe, while the other modes resemble the two-mode case).

Keywords: lead manganese telluride, lead telluride sulphide, structural properties, Raman spectroscopy.

INTRODUCTION

Due to its interesting physical properties, lead telluride has been studied intensively for more than 40 years. Its small band gap and high carrier mobilities identify it as a basic material for infrared optoelectronic devices¹ and thermoelectric materials in two-dimension quantum well systems.² PbTe crystallises in a rock-salt structure with a high ionic contribution to the bond energy.³ Lead-chalcogenides and their solid solutions have electrical active native point defects (vacancies and interstitial atoms) which produce energy states lying either above the bottom of the conduction band (donor defects) or below the top of the valence band (acceptors). This leads to a high charge car-

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rier concentration in undoped crystals because of the deviation of composition from stoichiometry. The pseudo-binary alloys PbTe–MnTe and PbTe–PbS are interesting materials for investigation in this field. These compounds were the subject of previous studies^{4–7} in which the influence of the concentration of impurities on structural and optical properties was investigated. In this paper, the results of Raman and X-ray measurements of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ ($x \leq 0.10$) and $\text{PbTe}_{1-x}\text{S}_x$ ($x \leq 0.05$) alloys are presented. Measurements on these samples at different temperatures give information about the positions of Mn (the cation side) and S (the anion side) in the lattice (off-centering), their clustering and ordering, as well as of the influence of these processes on the crystal structure and properties. A model of the phonon behaviour based on the Randon Element Isodisplacement model was applied in this study.

EXPERIMENTAL

The $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ ($x \leq 0.10$) crystals were grown by the Bridgman method with a lowering rate of 1 mm/h. The ingots had a diameter of 10 mm and a length about 50 mm. The chemical composition of the samples was controlled by an electron microprobe, which revealed good chemical homogeneity of the materials. The specimens were cut parallel to (100) (the cleavage plane) with an inner blade diamond cutter and then mechanically polished.

The $\text{PbTe}_{1-x}\text{S}_x$ single crystals were grown by the vapour–liquid technique (VLS), using metal and chalcogenide atoms of high purity as the source materials. The chemical composition of the samples was controlled by X-ray microprobe investigation.

The chemical composition of the products were also determined by the XRD powder technique. All the samples were examined under the same conditions, using a Siemens D500 powder diffractometer with Cu $K\alpha$, Ni-filtered radiation, in the diffraction angle range $2\theta = 25\text{--}100^\circ$.

The Raman spectra were taken with the 514.5 nm and 488 nm lines of an Ar laser (the average power was about 150 mW). A Jobin Yvon model U-1000 monochromator was used with a conventional photo-counting system. In order to attain a better signal-to-noise ratio, approximately 20 spectra were averaged.

RESULTS AND DISCUSSION

The unit cells of both $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ and $\text{Pb}_{1-x}\text{S}_x$ were calculated by the XRD powder technique using the least square method.^{5,6} As was already stated the structural properties of the $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ compounds were previously extensively investigated,⁵ where the obtained lattice constants agreed with the Vegard rule. The data for the end members were taken from the literature.⁸

The X-ray diffractogram for powdered $\text{PbTe}_{0.95}\text{S}_{0.05}$ is presented in Fig. 1. The refracting planes are denoted with (hkl) indices and correspond to literature data [JCPDS card number 381435] except for the reflection at $2\Theta \approx 38^\circ$ (denoted by *), which corresponds to PbS [JCPDS 200596]. $\text{PbTe}_{1-x}\text{S}_x$ is a pseudo-binary alloy (PbTe–PbS) with the rock salt structure, and a S content of 5 % was detected by the X-ray technique. As in the case of the $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ compounds, their lattice constants agree with the Vegard rule.

The unpolarized, room temperature Raman spectrum of a $\text{Pb}_{0.98}\text{Mn}_{0.02}\text{Te}$ single crystal in the spectral range of $15\text{--}200\text{ cm}^{-1}$ is presented in Fig. 2. The experimental results are presented by circles. The lines in Fig. 2 are the results of deconvolution. The

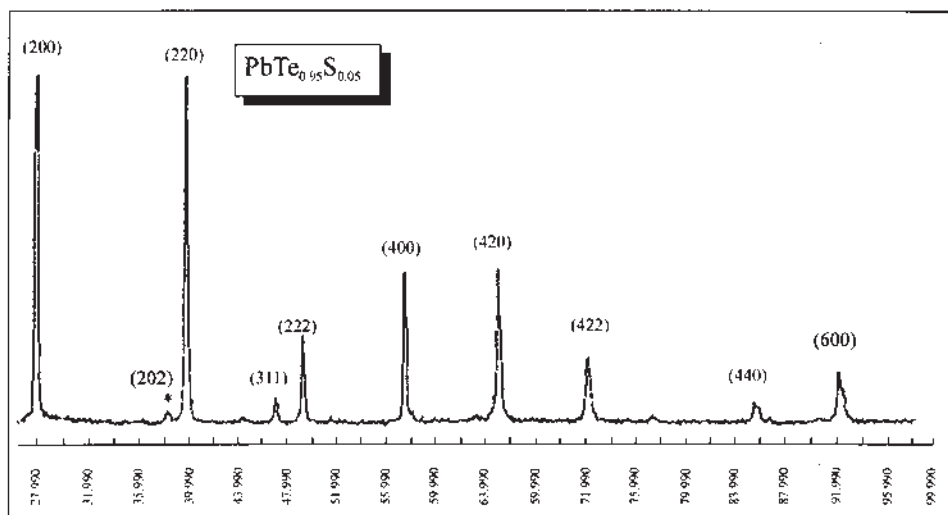


Fig. 1: X-Ray diffractogram of powdered PbTe_{0.95}S_{0.05}.

dashed line corresponds to the Rayleigh scattering. The two peaks at 129 and 146 cm^{-1} describe TeO₂ vibrational modes. For $x = 0.02$, two new modes at about 53 cm^{-1} and 104 cm^{-1} appeared. Decreasing the temperature had no influence on the intensity and position of the registered modes. On increasing the concentration to $x = 0.10$,⁹ the intensity of these modes increased, and their positions moved to 54 cm^{-1} and 115 cm^{-1} . The agreement between the experimental results and the convolution curve obtained in this way, is very good. The registered properties can be explained in the following manner: as is well known, PbTe crystallizes in a cubic structure of the NaCl Type (O_h space group symmetry), and the first-order Raman modes are not active. If the concentration of Mn is less than 12 %, Mn enters into the Pb sublattice as a substitutional impurity ion. As a consequence, a number of the Te-ions in PbTe are no longer in the centre of inversion symmetry, and PbTe vibrational modes could be Raman active (the impurity ion is still in the centre of the inversion, but its six nearest neighbours are not). Thus, the mode at about 104 cm^{-1} , the well known PbTe LO-like mode,¹⁰ become visible in the Raman spectra. In this way, the Mn²⁺ ions are still in the centre of inversion symmetry and Raman modes are not to be expected. However, this is in opposition with the experimental results.

The explanation for this discrepancy can be found by supposing that the Mn²⁺ ions in Pb_{1-x}Mn_xTe are off-centre. Off-centre-ion systems have been investigated in the literature.¹¹⁻¹³ The off-centering effect means that the impurity atoms are displaced from the regular lattice sites by about 0.5–1 Å, forming a permanent dipole and changing the local conditions in the lattice. It was found that the system has minimum energy when the small impurity ions are assumed to have off-centre positions along the (111) direction. It has been suggested¹² that an off-centre site is favoured when: (1) a large ionic size difference causes a decrease in the repulsive force because of reduced

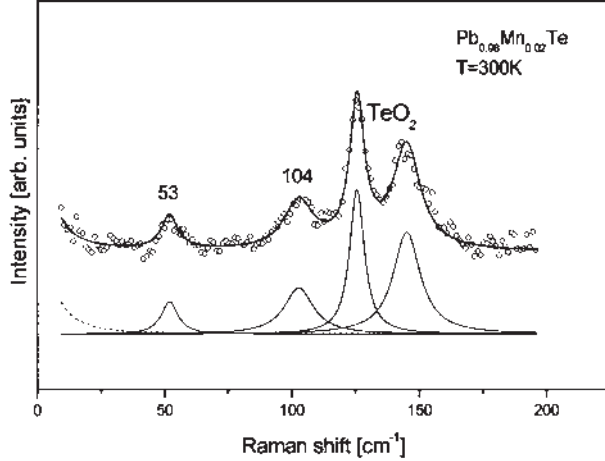


Fig. 2: Non-polarized Raman scattering spectrum of $\text{Pb}_{0.98}\text{Mn}_{0.02}\text{Te}$ crystal at room temperature.

ionic overlap, and (2) a large difference between the polarizability of the impurity ion and that of the lattice it replaces, resulting in a decrease of the polarization energy. This is based on the fact that the polarization force tends to drive the impurity ion towards the neighbour ions while the repulsive force tends to keep the impurity ion in the lattice site.¹³ The balance point of these two forces is the actual position of the impurity ion, which is displaced from the lattice site under these conditions. The replacement of Pb^{2+} ion by Mn^{2+} in $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ satisfies these conditions. $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ alloys have a large atomic-size mismatch between the substituted Mn atom and the host Pb atom (Mn^{2+} : 0.83 Å; Pb^{2+} : 1.18 Å). The difference between the ionic radii of Mn^{2+} and Pb^{2+} is about 0.35 Å. To the best of our knowledge, there are no exact data of Mn^{2+} polarizability in the literature. It was supposed¹⁴ on the basis of the known polarizabilities of Se^{2-} and MnSe that the polarizability of Mn^{2+} must be very small, about 1, as in the similar Fe^{2+} ion. The polarizability of the Pb^{2+} ion is 4.82, much larger than that for the Mn^{2+} ion which replaces it in the crystal lattice. According to Fig. 2, a dislocation of the Mn^{2+} ion from the central lattice position seems to be sufficient to break the selection rules. As a consequence, a mode at 53 cm^{-1} arises in the Raman spectra.

The non-polarized Raman spectra of $\text{PbTe}_{0.95}\text{S}_{0.05}$ in the spectral range from 25 to 220 cm^{-1} at temperatures between 20 and 300 K are shown in Fig. 3a. The experimental results are presented by circles. The full lines are the results of the application of deconvolution. A typical line shape obtained in this manner is shown in Fig. 3b. The dominant structures are clearly observed at about 40, 100 and a complex at about 150 cm^{-1} . These modes appeared as a consequence of the off-center position of the sulphur-atom, as in the case of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$. They represent the phonons of the $\text{PbTe}_{1-x}\text{S}_x$ solid solution and, as be seen later, it can be described by a modified Genzel model. At temperatures $T < 100$ K an additional mode at about 75 cm^{-1} was registered.

The temperature dependence of the mode at about 75 cm^{-1} is presented in Fig. 3c. The intensity of this mode is low at high temperatures. At a temperature of

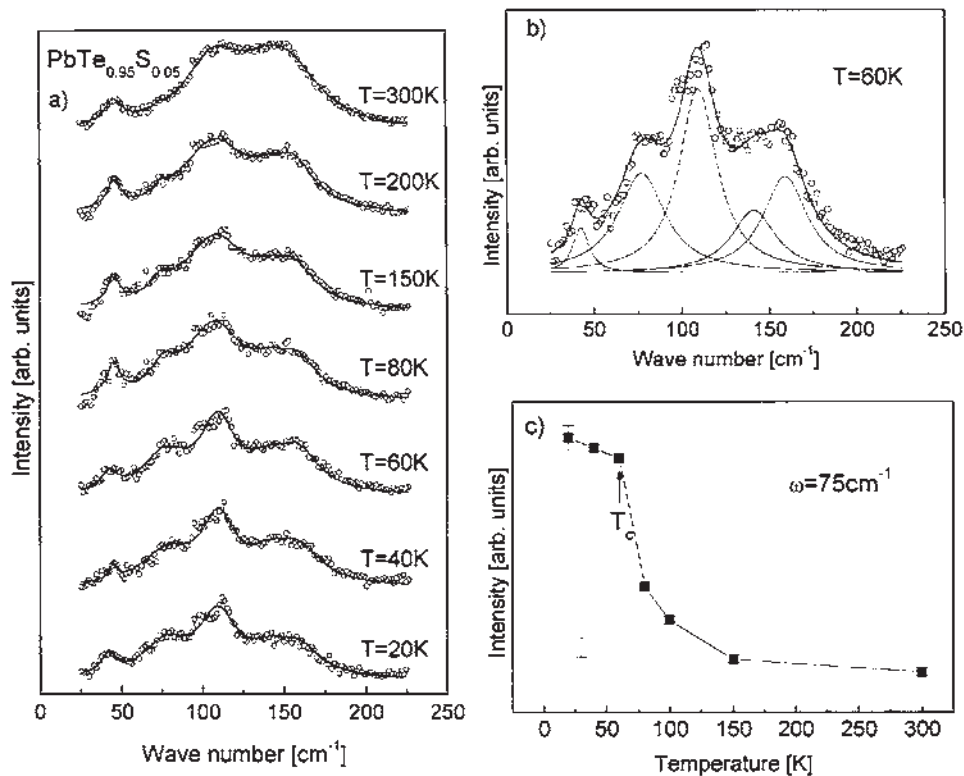


Fig. 3: a) Non-polarized Raman scattering spectra of PbTe_{0.95}S_{0.05} crystal at different temperatures; b) Deconvolution of the spectrum of PbTe_{0.95}S_{0.05} at $T = 60$ K; c) Temperature dependence of the intensity of the mode at 75 cm^{-1} .

about 100 K a slow increase of the intensity of the mode was observed. At $T \approx 60$ K, the intensity of the mode was almost three times higher. With further decrease of the temperature, the increase of the mode intensity is weak and hardly noticeable. This kind dependency of the mode intensity on temperature in the case of the other PbTe based systems is assumed to be the consequence of the already described off-center phenomena of sulphur in PbTe_{1-x}S_x. At "high" temperatures, the off-centers are randomly oriented, so the mode intensity connected with them is low. Ordering of the off-centers and electrical dipoles during the phase transition affect the crystal polarizability, and the intensity of this mode increases. This kind of behaviour is stable above the temperature $T = 60$ K for the sample with $x = 0.05$, and further decreasing of the temperature does not affect the intensity of this mode. The position of the off-center ion in PbTe_{1-x}S_x is presented in Fig. 4. In the case of Pb_{1-x}Mn_xTe, this type of phase transition was not observed, and this phonon does not appear and consequently, there is not temperature dependence.

To study the mode of behaviour of a phonon for the ternary compounds Pb_{1-x}Mn_xTe and PbTe_{1-x}S_x, a model based on the Genzel model¹⁵ was applied and then the agree-

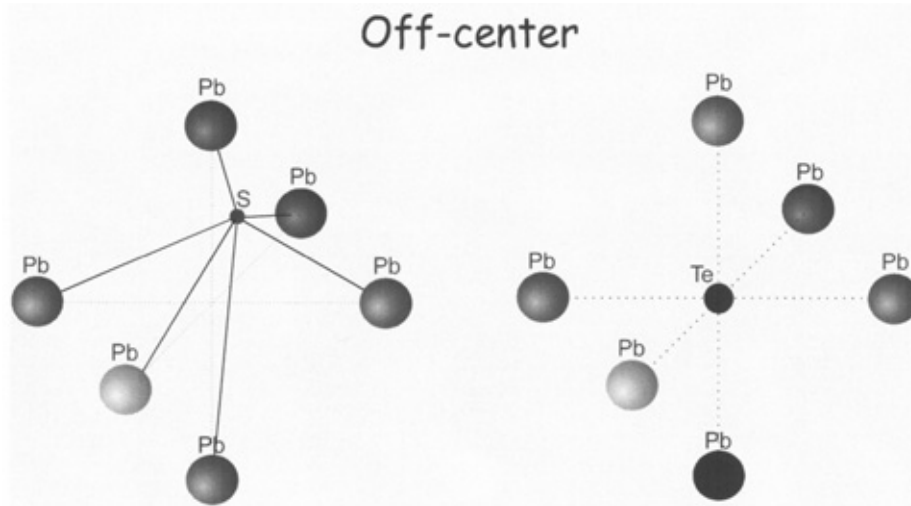


Fig. 4: Position of the off-center ion in $\text{PbTe}_{1-x}\text{S}_x$.

ment between the theoretical and experimental results was checked. This model gave good results in previous studies¹⁶⁻¹⁹ for describing the phonon behaviour in the ternary ($\text{Hg}_{1-x}\text{Mn}_x\text{Te}$, $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$) and quaternary ($\text{Cd}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$, $\text{Hg}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$) mixed crystals. In the calculations, the basic assumptions of the Random Element Isodisplacement model (REI) model²⁰ were employed. Namely, in the $\text{A}_{1-x}\text{B}_x\text{C}$ type of mixed crystals, the crystal lattice of a mixed system comprises two sublattices, one of them filled by C atoms only and the second filled by A and B atoms, randomly distributed. The local electric field (E_{loc}) was taken into account and a connection between the microscopic and macroscopic parameters was made using the Born-Huang procedure,²¹ where the dependence of the force constant between first neighbours on concentration (x) was neglected but the second-neighbour force constant were involved. The concentration dependence of the optical mode frequencies of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$

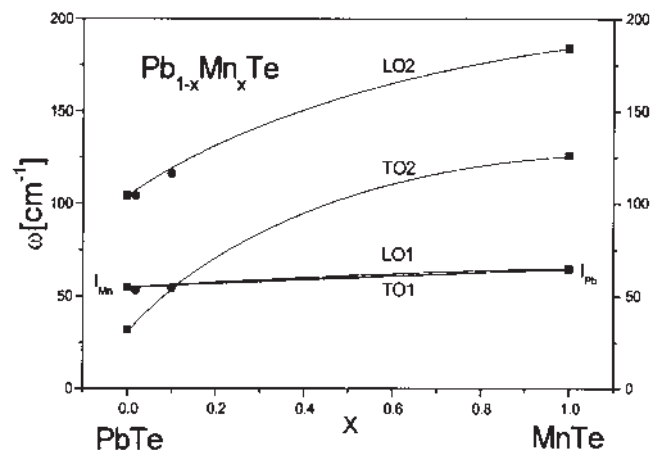


Fig. 5: Concentration dependence of the frequency of the optical modes of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ single crystals.

and PbTe_{1-x}S_x single crystals are presented in Figs. 5 and 6. The curves shown in Figs. 5 and 6 were obtained by this model. The experimental values for the TO and LO modes are marked by full circles while the values taken from the literature,⁸ by full squares. The agreement between the experimental and theoretical results is very good, with regards to the approximations on which these models are based.

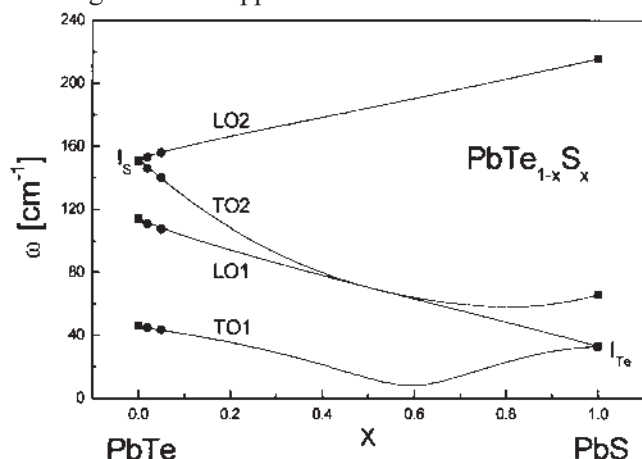


Fig. 6: Concentration dependence of the frequency of the optical modes of PbTe_{1-x}S_x single crystals.

The results shown in Figs. 5 and 6, suggest that the phonons in PbTe_{1-x}S_x show the two-mode behaviour (each TO–LO mode pair of the end members degenerates to an impurity mode), while the Pb_{1-x}Mn_xTe optical phonons have an intermediate one-two-mode behaviour (the LO-mode frequency shift continuously from PbTe to MnTe, while the other modes resemble the two-mode case).

CONCLUSION

The appearance of new Raman active modes in Pb_{1-x}Mn_xTe and PbTe_{1-x}S_x crystals is satisfactorily explained by the existence of off-centre in these compounds. It was also found that the phonons in PbTe_{1-x}S_x show two-mode behaviour, while the Pb_{1-x}Mn_xTe optical phonons have an intermediate one-two-mode character.

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ИЗВОД

Pb_{1-x}Mn_xTe и PbTe_{1-x}S_x ЈЕДИЊЕЊА И ЊИХОВЕ ОПТИЧКЕ ОСОБИНЕ

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Кристали Pb_{1-x}Mn_xTe су добијени методом по Бридгман-у, а кристали PbTe_{1-x}S_x су расли помоћу технике гасовито–течно–чврсто. Структурне особине Pb_{1-x}Mn_xTe (x ≤ 0,10) и PbTe_{1-x}S_x (x ≤ 0,05) су посматране рендгенском дифракцијом праха. Оптичке особине су

проучаване на различитим температурама помоћу Raman спектроскопије. Мерења на различитим концентрацијама дају одговоре о положајима Mn и S у решетки (off-центри-ма), њиховом кластеровању, поретку као и о њиховом утицају на структуру и особине кристала. Примењен је модификовани REI модел за понашање фонона код чврстих раствора и нађено је да фонони у $\text{PbTe}_{1-x}\text{S}_x$ показују дво-модно понашање (сваки TO–LO мод крајњих чланова се дегенерише у примесни мод), док $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ оптички фонони имају интермедијално једно-дво-модно понашање (фреквенција LO-мода се континуално помера од PbTe ка MnTe, док други модови задржавају дво-модно понашање).

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