

# Determination of Tm Charge State in PbTe(Tm) by XANES Method

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## Abstract

The local environment and the charge state of Tm atoms in PbTe were studied by EXAFS and XANES techniques at the L<sub>III</sub> absorption edge of Tm (8.648 keV). It was revealed that Tm atoms predominantly substitute for Pb atoms in PbTe and are surrounded by Te atoms at a distance of  $2.99 \pm 0.02 \text{ \AA}$ . Tm atoms were found to be in Tm<sup>3+</sup> charge state independently of the section of the phase diagram used for Tm doping. These results are in agreement with the results of previous investigation of the Pb-Tm-Te phase diagram.

Electrical studies of PbTe(Tm) with large deviation from stoichiometry revealed that the electron concentration was about one order of magnitude lower than the total Tm concentration and remained nearly constant (about  $10^{19} \text{ cm}^{-3}$ ) while varying the sample composition. Reduced electrical activity of the Tm impurity in PbTe was explained by effect of selfcompensation.

## 1. Introduction

Narrow-gap IV-VI semiconductors have attracted considerable attention due to their wide application in infrared (IR) optoelectronics. They are mainly used for production of photodiodes and photoresistors, as well as for lasers, working in middle and far IR regions. At the present time the development of new types of photodetectors is closely connected with utilizing of unusual impurity effects recently discovered in doped IV-VI semiconductors. The study of impurity states created by doping of these semiconductors with some of III-group elements [1], transition [2] and rare-earth metals [3], each of which can have several charge states, revealed unusual physical properties, such as the pinning of the Fermi level and giant IR photoconductivity. The appearance of these effects in PbTe(In) was attributed to the In<sup>+</sup>-In<sup>3+</sup> valence switching [4]. It should be noted, that if the doping impurities have magnetic moment, the doped semiconductor may exhibit interesting magnetic properties [2, 3].

It is well known that Tm atom in thulium chalcogenides can also exist in two charge states (Tm<sup>2+</sup> and Tm<sup>3+</sup>) or exhibit intermediate valence [5–9]. Thulium ion is divalent in bulk stoichiometric TmTe [9] and trivalent in bulk TmS [6], while in thin surface layer of TmS the Tm ion is divalent [6, 7]. The transition from Tm<sup>2+</sup> to Tm<sup>3+</sup> in bulk materials may be related to an increase of splitting of 5d states in a crystal field with the decrease of the lattice parameter, which results in disappearing of energy gap in the case of TmS. In Tm<sub>2</sub>Te<sub>3</sub> [9] as well as in Tm<sub>2</sub>O<sub>3</sub> [10] Tm atom is in trivalent state. It should be noted that the lattice parameter in TmTe is larger than in Tm<sub>2</sub>Te<sub>3</sub>, so the transition from Tm<sup>2+</sup> state in TmTe to Tm<sup>3+</sup> state in Tm<sub>2</sub>Te<sub>3</sub> can be explained in a similar way. The pressure, temperature and

component concentration are also the factors, which can affect the charge state of Tm in compounds and solid solutions [11]. The anion radius of Se<sup>2-</sup> and the lattice parameter in TmSe have intermediate values between the corresponding data for TmS and TmTe and, therefore, the charge state of Tm in TmSe is difficult to predict from simple reasons. Based on experimental data, the authors of [8] came to a conclusion that Tm has a mixed valence in bulk TmSe.

As follows from all the above, thulium impurity in PbTe may have different valence, and so we decided to carry out direct measurements of the Tm charge state in Tm-doped PbTe and to compare the results with those obtained from electrical measurements on these solid solutions.

XAFS spectroscopy is known to be a powerful tool for studies of the charge state and local environment of rare-earth atoms with different valence in compounds and solid solutions. XAFS technique has two main advantages:

- 1) it can measure directly the ratio of number of ions in different charge states by analyzing the structure of the spectrum near the absorption edge;
- 2) it enables to obtain the instantaneous radial distribution function of the distances to neighbors of possibly unstable (in valence) ions from the analysis of EXAFS data.

Strong white lines at the absorption edge distinguish the L<sub>III</sub> X-ray absorption spectra of the rare-earth metals. These lines arise from transitions from atomic 2p<sub>1/2</sub> (L<sub>II</sub>) and 2p<sub>3/2</sub> (L<sub>III</sub>) levels into partially filled large density d states. The shape and structure of these lines depend on the electron configuration and charge state of the atom. Therefore the study of these lines can give information on charge states, in particular, charge state of the Tm atom in PbTe. XANES and EXAFS techniques have been already used for investigation of the charge states and local environment of Tm atoms in all thulium monochalcogenides [12, 13] and some their solid solutions [10]. XAFS spectroscopy data confirmed that Tm is divalent in TmTe, Tm is trivalent in TmS, but in TmSe it exhibits an intermediate valence state in the bulk and the divalent state at surface [10, 12]. The value of bulk mean valence in TmSe was shown to be sensitive to the stoichiometry of samples.

To our knowledge, there are only few published XAFS data on the charge state of the Tm impurity in other crystals, besides monochalcogenides. Detailed results on ZnS(Tm) [14] and CaSO<sub>4</sub>(Tm) [15] are only available. Although lead chalcogenides have received particular attention, the systematic study of the impurity charge states in them by X-ray absorption was not undertaken yet.

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In this paper we present new results on EXAFS, XANES and electrical studies of Tm-doped PbTe.

## 2. Samples and experimental

All measurements were carried out on polycrystalline samples and single crystals of PbTe(Tm).

XANES measurements on PbTe(Tm) were performed on single crystals grown by Bridgman method along the PbTe-TmTe and PbTe-Tm<sub>2</sub>Te<sub>3</sub> sections of the phase diagram and on polycrystalline samples of TmTe, Tm<sub>2</sub>Te<sub>3</sub> and Tm<sub>2</sub>O<sub>3</sub>. The concentrations of thulium in PbTe(Tm) were 0.85 and 3.0 at.%, correspondingly. The samples were synthesized from binary compounds PbTe, TmTe or Tm<sub>2</sub>Te<sub>3</sub> in evacuated quartz ampoules. Before XANES measurements the crystals were powdered in argon atmosphere and placed into a special argon-filled camera. Argon atmosphere prevented the oxidation of samples, the manifestation of which was detected in our previous EXAFS study of Tm-doped PbTe samples. All single crystals of PbTe(Tm) had the NaCl crystal structure, while Tm chalcogenides had either the NaCl structure (for TmTe) or the NaCl-based superstructure (defect NaCl structure with Tm vacancies of the Sc<sub>2</sub>S<sub>3</sub> type for Tm<sub>2</sub>Te<sub>3</sub>) at 300 K. Oxide Tm<sub>2</sub>O<sub>3</sub> had the Mn<sub>2</sub>O<sub>3</sub> structure at 300 K.

EXAFS measurements on PbTe(Tm) were performed on the samples grown by Bridgman method along the PbTe-TmTe sections of the phase diagram. The Tm concentrations in Tm-doped PbTe were 3.0 and 5.0 at.%. It should be noted that no special efforts were undertaken to prevent the sample oxidation in this EXAFS experiment.

Electrical measurements were performed on a series of polycrystalline PbTe(Tm) samples with different deviation from stoichiometry. The samples were prepared by alloying the beforehand synthesized (PbTe)<sub>0.985</sub>(Tm<sub>2</sub>Te<sub>3</sub>)<sub>0.015</sub> compound with extra lead or tellurium in evacuated quartz ampoules. Concentration of Tm in all these samples was 3.0 at.%. The samples were annealed at 800 °C for 60 hours.

EXAFS experiments were carried out on station 7.1 of the synchrotron radiation source of Daresbury Laboratory (UK) with an electron beam energy of 2 GeV and maximum storage ring current 250 mA. The synchrotron radiation was monochromatized by two flat Si (111) crystals. Spectra were measured at the L<sub>III</sub> absorption edge of Tm (8.648 keV) in fluorescence mode at 300 K. Before EXAFS measurements the samples were powdered, the powders were sifted through a sieve and then rubbed onto the surface of adhesive tape. The thick-sample limit for the fluorescence measurements was achieved by folding the tape (8...16 layers). More detailed description of the experiment and EXAFS spectra processing can be found elsewhere [16].

XANES data were collected on EXAFS station at VEPP-3 (Novosibirsk, Russia) with an electron beam energy of 2 GeV and maximum storage ring current 100 mA. Measurements were performed at 300 K at the L<sub>III</sub> absorption edge of Tm in fluorescence mode in oxygen-free atmosphere. The standards for Tm<sup>2+</sup> and Tm<sup>3+</sup> valence states were TmTe, Tm<sub>2</sub>Te<sub>3</sub> and Tm<sub>2</sub>O<sub>3</sub>.

The measurements of conductivity and Hall effect were done by standard technique on rectangular-shaped samples with typical dimensions of 4 × 1 × 5 mm<sup>3</sup> at room temperature. The current and potential contacts to the samples were soldered by indium.

## 3. Results and discussion

Figure 1 shows the EXAFS spectrum for Pb<sub>0.95</sub>Tm<sub>0.05</sub>Te sample obtained at the Tm L<sub>III</sub> edge. The analysis of the first shell

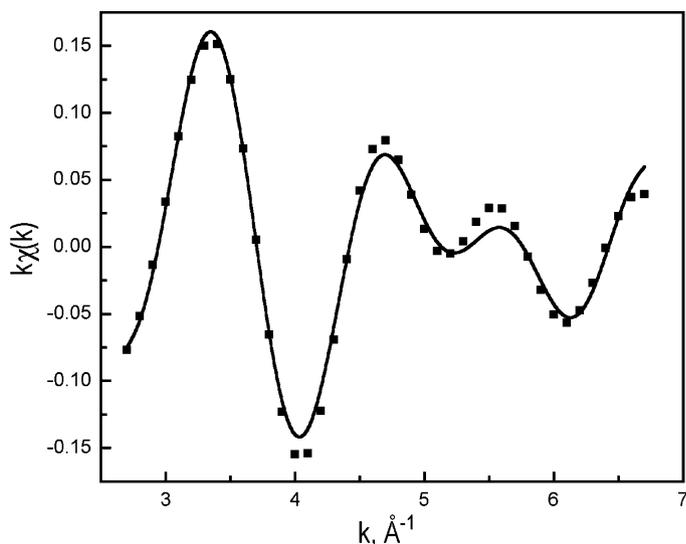


Fig. 1. EXAFS data corresponding to the first shell of Pb<sub>0.95</sub>Tm<sub>0.05</sub>Te obtained at the Tm L<sub>III</sub> edge at 300 K. Points are experimental data and the line is its best theoretical approximation.

revealed that Tm atoms substitute for the metal atoms in PbTe and are surrounded by tellurium atoms at a distance of  $2.99 \pm 0.02$  Å. Moreover, in the first shell a contribution from the atoms, located at  $2.26 \pm 0.02$  Å was found. The comparison of the obtained distances with known bond lengths in TmTe [12], Tm<sub>2</sub>Te<sub>3</sub> [13] and Tm<sub>2</sub>O<sub>3</sub> [17] compounds showed that, apparently, Tm atoms in PbTe are in the trivalent state, that is indicated by negligible difference in distances of Tm-Te in PbTe(Tm) (2.99 Å) and Tm-Te in Tm<sub>2</sub>Te<sub>3</sub> (3.02 Å). Concerning the atoms located in the first shell at a distance of 2.26 Å, one can see that this distance is close to mean Tm-O distance in Tm<sub>2</sub>O<sub>3</sub> (2.25 Å). Therefore we think that, except Te, the oxygen atoms are also present in first shell of Tm. The appearance of oxygen in our samples may be a result of oxidation of samples during their synthesis, preparation and measurement.

In spite of the presence of oxygen in the samples, the conclusion that Tm impurity atoms in PbTe substitute predominantly for Pb atoms is still valid. However, uncontrolled oxidation may prevent the reliable determination of the charge state of Tm in PbTe. That is why we decided to carry out additional XANES measurements in oxygen-free atmosphere with a special care to prevent oxidation during the sample preparation.

Figure 2 presents the XANES spectra for two samples of PbTe(Tm) with different Tm concentration, as well as for TmTe and Tm<sub>2</sub>Te<sub>3</sub> compounds. It is seen that the L<sub>III</sub> absorption edge of Tm is denoted by a strong white line. This line is in fact a general feature of L<sub>III</sub> edges for all rare-earth atoms in 2+ and 3+ valence states and is mainly due to transitions into empty 5d state. As follows from this figure, the spectra corresponding to the different electron configurations and charge states of Tm, differ considerably. The edge structure of Tm in Tm<sub>2</sub>Te<sub>3</sub> (Tm<sup>3+</sup> charge state) consists of one strong white line. The same structure was observed in Tm<sub>2</sub>O<sub>3</sub>. The XANES spectra of Tm in TmTe (Tm<sup>2+</sup> charge state) have characteristic doublet structure, in which the long-wavelength white line has nearly the same shape as that of Tm<sup>3+</sup> in Tm<sub>2</sub>Te<sub>3</sub>, but is shifted by nearly 8 eV towards lower energy.

Comparative analysis of spectra obtained for Tm-doped PbTe crystals and standard samples leads to a conclusion that Tm

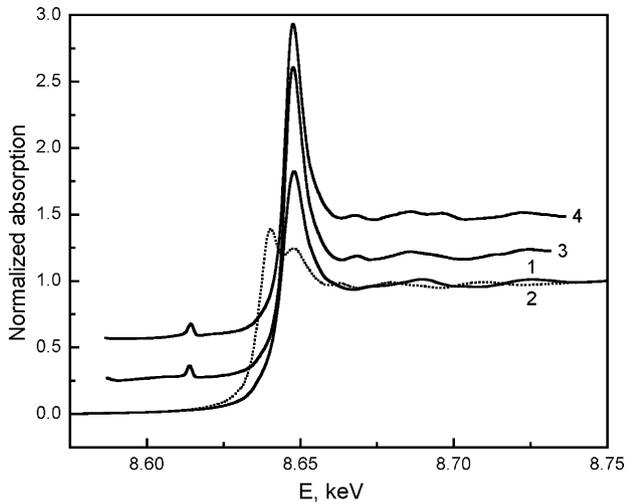


Fig. 2. Normalized XANES spectra obtained at the Tm  $L_{III}$  edge for  $Tm_2Te_3$  (1),  $TmTe$  (2),  $PbTe-Tm_2Te_3$  solid solution (3) and  $PbTe-TmTe$  (4) solid solution at 300 K.

atoms in  $PbTe$  are in the  $Tm^{3+}$  charge state independently of the section of the phase diagram used for Tm doping. Indeed, in XANES spectra for  $PbTe(Tm)$  we failed to detect even the minor contribution of the second line observed for  $Tm^{2+}$  states. This result is in agreement with the data of our EXAFS measurements and the results of the  $Pb-Tm-Te$  phase diagram investigation [18], which established that the  $PbTe-TmTe$  section of the phase diagram is not quasibinary and at high Tm concentration in samples the  $Pb$  precipitations may even arise.

Data obtained from EXAFS and XANES spectra give evidence that Tm atoms in  $PbTe$  substitute for  $Pb$  atoms and are in the trivalent state and, therefore, must play a role of a single charged donor in these crystals. This conclusion was confirmed by our electrical measurements. Indeed, all investigated  $PbTe(Tm)$  samples had n-type conductivity; however, the expected direct relation between Tm and free carrier concentrations in the samples was not found. Measured electron concentration was about one order of magnitude lower than the value expected for single charged donors. To study the origin of this discrepancy, additional experiments on non-stoichiometric samples were performed.

Assuming the single charged donor behavior of the Tm atom, one could expect that addition of extra  $Pb$  within the homogeneity region of  $PbTe(Tm)$  would result in an increase of free electron concentration, while the addition of extra  $Te$  would decrease it. The dependence of the carrier concentration on the deviation from the stoichiometry is shown in figure 3. It is seen that the electron concentration remains nearly constant when varying the sample composition. There are two ways to explain these results.

The first explanation is the pinning of the Fermi level by Tm impurity, by analogy with the action of the In impurity. In the case of indium the In atoms are present simultaneously in both charge states ( $In^+$  and  $In^{3+}$ ) and the addition of extra  $Pb$  or  $Te$  changes only their relative concentrations. The pinning of the Fermi level in this case is provided by  $In^+$  ions, which are negative-U centers (centers with negative correlation energy). However, the supposition that Tm has the same properties in  $PbTe$  disagrees with our XANES data, which indicates the existence of only one charge state of Tm.

The second explanation of the obtained dependence of the carrier concentration on the composition supposes that the donor

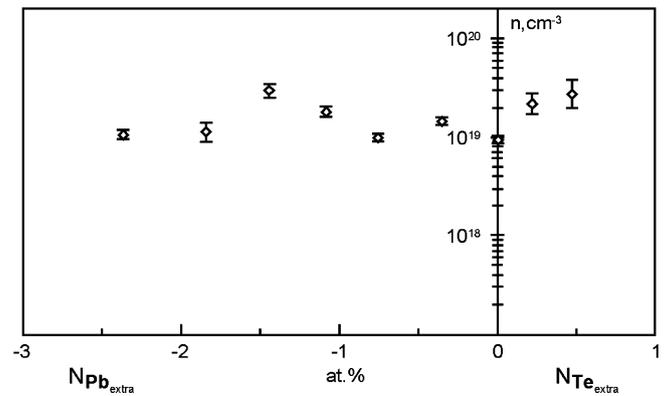


Fig. 3. Dependence of the electron concentration on the deviation from the stoichiometry for  $Pb_{0.97}Tm_{0.03}Te$  samples at 300 K.

action of Tm is compensated by the acceptor behavior of intrinsic defects in  $PbTe$ , such as  $Pb$  vacancies. It is known that the doping of lead chalcogenides with high concentration of I, Cl, In or Ga donor impurities results in an increase (by more than one order of magnitude) in solubility of extra stoichiometric  $Te$ , while doping them with Tl or Na acceptor impurities leads to an increase in solubility of excess  $Pb$  [19–21]. The nature of such a selfcompensation effect is that the doping of a sample with electrically active impurities makes it energetically favorable the formation of intrinsic point defects that have an opposite electrical sign. Due to selfcompensation, the change of the carrier concentration is always smaller than the concentration of the doping impurities. In our opinion this explanation seems to be more preferable.

#### 4. Conclusions

In conclusion, the X-ray absorption and electrical studies of Tm-doped  $PbTe$  crystals revealed that Tm atoms predominantly substitute for  $Pb$  atoms and are in  $Tm^{3+}$  charge state independently of the section of the phase diagram used for Tm doping. This conclusion is in agreement with the results of investigation of the  $Pb-Tm-Te$  phase diagram. Reduced electrical activity of Tm impurity in  $PbTe$  is explained by the effect of selfcompensation.

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