Abstract

The local environment and the charge state of Tm atoms in PbTe were studied by EXAFS and XANES techniques at the LIII 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 ± 0.02 Å. Tm atoms were found to be in Tm$^{2+}$ 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$^{19}$ cm$^{-3}$) while varying the sample composition. Reduced electrical activity of the Tm impurity in PbTe was explained by effect of self-compensation.

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

A. I. Lebedev, I. A. Sluchinskaya, S. G. Nikitenko and S. G. Dorofeev

1Department of Physics, Moscow State University, Leninskie gory, 119899 Moscow, Russia
2Institute of Catalysis, 630090 Novosibirsk, Russia
3Chemistry Department, Moscow State University, Leninskie gory, 119899 Moscow, Russia

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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 photo-diodes 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$^{2+}$-In$^{3+}$ 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 atoms in thulium chalcogenides can also exist in two charge states (Tm$^{2+}$ and Tm$^{3+}$) 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$^{2+}$ to Tm$^{3+}$ 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 TmTe [9] as well as in Tm$_2$O$_3$ [10] Tm atom is in trivalent state. It should be noted that the lattice parameter in TmTe is larger than in Tm$_2$O$_3$, so the transition from Tm$^{2+}$ state in TmTe to Tm$^{3+}$ state in Tm$_2$O$_3$ 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$^{-2}$ 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 LII X-ray absorption spectra of the rare-earth metals. These lines arise from transitions from atomic 2p$^1$/2 (LII) and 2p$^3$/2 (LIII) levels into partially filled large density of 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 monochalco-genides [12, 13] and some of their solid solutions [10]. XAFS spectroscopy data confirmed that Tm is divalent in TmTe, Tm is trivalent in TmSe, but in TmS 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 monochalco-genides. Detailed results on ZnS(Tm) [14] and CaSO$_4$(Tm) [15] are only available. Although lead chalco-genides have received particular attention, the systematic study of the impurity charge states in them by X-ray absorption was not undertaken yet.

*E-mail: Irmasha1@tmm.ru
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-Tm2Te3 sections of the phase diagram and on polycrystalline samples of TmTe, Tm3Te4 and Tm2O3. The concentrations of tellurium in PbTe(Tm) were 0.5, 5.0, and 15.0 at. %, correspondingly. The samples were synthesized from binary compounds PbTe, TmTe or Tm2Te3 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 ScS3 type for Tm2Te3) at 300 K. Oxide Tm2O3 had the Mn2O3 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)n+(TmTe)bOc (n=3, b=4, c=5) compound with 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 100 mA. Measurements were performed at 300 K at the LIII absorption edge of Tm (8.648 keV) in fluorescence mode at an electron beam energy of 2 GeV and maximum storage ring current (8...16 layers). More detailed description of the experiment and XANES data 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 LIII absorption edge of Tm in fluorescence mode in oxygen-free atmosphere. The standards for Tm3+ and Tm5+ were TmTe, Tm3Te4 and Tm2O3.

The measurements of conductivity and Hall effect were done by standard technique on rectangular-shaped samples with typical dimensions of 4 × 1 × 5 mm3 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 Pb0.95Tm0.05Te sample obtained at the Tm LIII edge. The analysis of the first shell revealed that Tm atoms substitute for the metal atoms in PbTe and are surrounded by tellurium atoms at a distance of 2.99 ± 0.02 Å. Moreover, in the first shell a contribution from the atoms, located at 2.26 ± 0.02 Å was found. The comparison of the obtained distances with known bond lengths in TmTe [12], Tm3Te4 [13] and Tm2O3 [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 Tm2Te3 (2.26 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 Tm2O3 (2.5 Å). Therefore we think that, except Tc, the oxygen atoms are also present in first shell of Tm.

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 Tm2Te3 compounds. It is seen that the LIII absorption edge of Tm is denoted by a strong white line. This line is in fact a general feature of LIII edges for all rare-earth atoms in 2+ and 3+ valence states and is mainly due to transitions into empty 4f shells of the corresponding electrons. 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 Tm2Te3 (Tm3+ charge state) consists of one strong white line. The same structure was observed in Tm2O3. The XANES spectra of Tm in PbTe (Tm2+ charge state) have characteristic doublet structure, in which the long-wavelength white line has nearly the same shape as that of Tm3+ in Tm2Te3, 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...
The dependence of the carrier concentration on the deviation from TmTe (2), PbTe-Tm2Te3 solid solution (3) and PbTe-TmTe (4) solid solution at 300 K.

Data obtained from EXAFS and XANES spectra give evidence that Tm atoms in PbTe substitute for Pb atoms and are in the Tm3+ 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 Tm2+ 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 quasistable and at high Tm concentration in samples the Pb precipitations may even arise.

The second explanation of the obtained dependence of the carrier concentration on the stoichiometry for PbTe(Tm) samples at 300 K.

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 Tm3+ 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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References

17. ICSD database (CD ROM version).