

Detection of impurity states in the photoluminescence spectra of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ ($x \sim 0.2$) solid solutions

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We have observed that the photoluminescence spectra of cadmium- or indium-doped solid solutions $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ ($0.18 \leq x \leq 0.22$) contain emission lines due to the impurities in addition to those of band-to-band transitions. Heavy doping with cadmium leads to the formation of a four-component solid solution with deep impurity levels.

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There are a number of interesting electrical and optical properties¹⁻³ observed in indium-doped $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solutions. We have discovered that the photoluminescence spectra of the solid solution $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ with Cd and In impurities contain radiation due to the impurities as well as radiation due to band-to-band transitions. The emission lines due to cadmium had an energy less than the band gap E_g , while those due to indium had an energy about twice as large as the band gap E_g of the undoped semiconductor.

The photoluminescence spectra were measured at temperatures between 2 and 77 K in epitaxial layers of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ ($0.18 \leq x \leq 0.22$) grown on (100) PbTe substrates by the method of liquid-phase epitaxy and on (111) BaF_2 substrates by the method of instantaneous evaporation in vacuum. The impurity concentrations varied between 8×10^{17} and $4 \times 10^{19} \text{ cm}^{-3}$ for the indium-doped samples and from $\sim 10^{19}$ to $\sim 10^{21} \text{ cm}^{-3}$ for the cadmium-doped samples. Excitation was provided by either a pulsed YAG:Nd³⁺ ($h\nu \simeq 1.2 \text{ eV}$) or CO ($h\nu \simeq 0.23 \text{ eV}$) laser.

The introduction of cadmium to a $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solution leads to three basic effects: 1) the band gap E_g increases as the cadmium concentration N_{Cd} increases. This increase of E_g can reach $\sim 50\%$. 2) The intensity of the photoluminescence at first increases N_{Cd} is increased (by about a factor of five for $N_{\text{Cd}} \sim 10^{20} \text{ cm}^{-3}$), then falls off. 3) On the long-wavelength side of the emission from band-to-band transitions there are two weak lines, which we call *A* and *B*, in the cadmium-doped material (Fig. 1a). These lines are observed at relative high ($\gtrsim 10^3 \text{ W/cm}^2$) levels of excitation and at temperatures from 2 to $\sim 30 \text{ K}$. The intensity of lines *A* and *B* is two or three orders of magnitude (depending on the cadmium concentration) smaller than the intensity of the band-to-band transitions and increases almost linearly with the level of excitation. The intensity of line *B* is usually three to six times as great as the intensity of line *A*. The width of lines *A* and *B* depends weakly on temperature and increases with increasing cadmium concentration, changing from 1.7 to 3.2 meV. The band gap of E_g and the energy of lines *A* and *B* as functions of the cadmium concentration are shown in Fig. 2. It is seen that E_g increases markedly under cadmium doping and that the energy

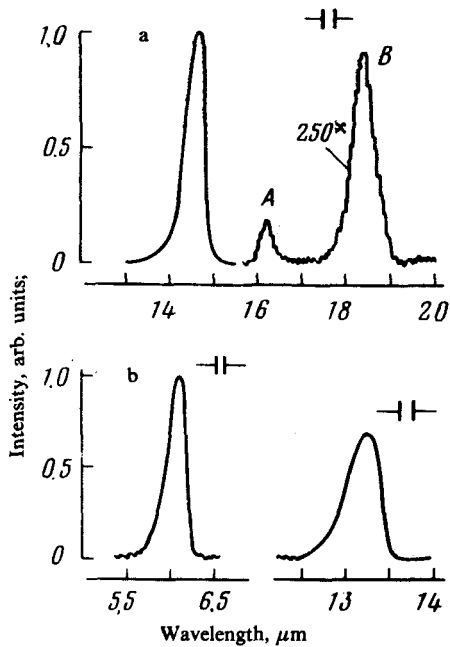


FIG. 1. Photoluminescence spectra of doped $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ layers: a) $x \approx 0.20$, $N_{\text{Cd}} \sim 10^{20} \text{ cm}^{-3}$, $T = 4.2 \text{ K}$, intensity of CO-laser excitation $I = 1.5 \times 10^4 \text{ W/cm}^2$; b) $x \approx 0.18$, $N_{\text{IN}} \sim 10^{18} \text{ cm}^{-3}$, $T = 20.4 \text{ K}$, intensity of YAG-laser excitation $I = 6 \times 10^4 \text{ W/cm}^2$.

margin $E_g - h\nu$ at concentrations of $\sim 10^{19} \text{ cm}^{-3}$ is about twice as large for line B as for line A.

Undoped $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ ($x \sim 0.2$) layers have the usual p -type conductivity, which is due to metal vacancies in the lattice. The concentration of holes (metal vacancies) can amount to 10^{17} to 10^{20} cm^{-3} , depending on the conditions of growth. Cadmium doping reduces the concentration of holes and can reverse the type of conductivity (at

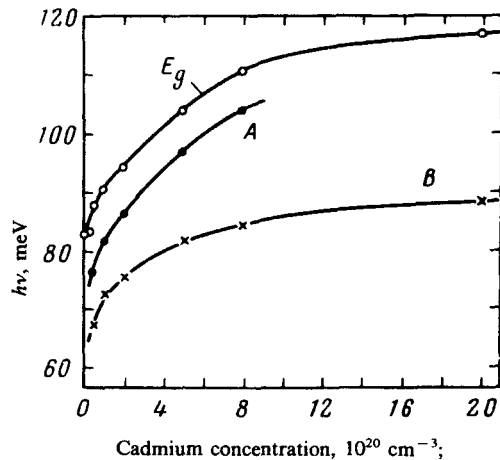


FIG. 2. Energy position of photoluminescence lines as a function of the cadmium concentration for a $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$ sample.

$N_{Cd} \sim 10^{19} \text{ cm}^{-3}$).

It has been shown^{4,5} that not all of the positively charged atoms are active, but only those occupying negatively charged metal vacancies. Most of the introduced atoms are neutral and occupy interstitial sites in the lattice. We assume that the most probable locations of the atoms are such that they are found in a tetrahedral environment in the tellurium sublattice. This structure is analogous to that of the wide-band semiconductor CdTe. This hypothesis and the fact that E_g changes strongly as the cadmium concentration is increased permit the conclusion that the electrically active cadmium atoms heal point defects in the material and thereby increase the quantum yield of the luminescence, while the neutral cadmium atoms lead to the formation of a four-component solid solution PbTe–SnTe–CdTe.

It should be noted that the formation of a four-component solid solution becomes noticeable in the luminescence spectra at cadmium concentrations as low as $\sim 10^{19} \text{ cm}^{-3}$. This means that one can determine the cadmium concentration from the change in E_g beginning at $\sim 0.1 \text{ at.}\%$. We measured the line shape of the edge emission and the splitting of the line in a quantizing magnetic field by a method analogous to that of Ref. 6. The measurements showed that the transitions are band-to-band transitions, at least at concentrations of up to $\sim 10^{20} \text{ cm}^{-3}$.

The neutral cadmium atoms play another role as well: they are effective capture centers for the secondary charge carriers (i.e. holes). In fact, in cadmium-doped samples at low temperatures it has been observed⁷ that the lifetime of the electrons is two or three orders of magnitude lower than that of the holes. Inasmuch as the cadmium atoms can be found in two charge states (Cd^+ and Cd^{++}), they should have two levels for radiative capture of electrons from the conduction band. A proposed scheme for the radiative transitions in PbTe–SnTe–CdTe is shown in Fig. 3. The cadmium levels are deep, since the ionization energy of hydrogen-like and exciton states in type $A^{IV}B^{VI}$ semiconductors is very small ($\lesssim 10^{-4} \text{ eV}$).

For indium-doped layers the intensity of the photoluminescence under excitation by a CO laser decreases markedly: for $N_{In} \sim 10^{18} \text{ cm}^{-3}$ the intensity is an order of

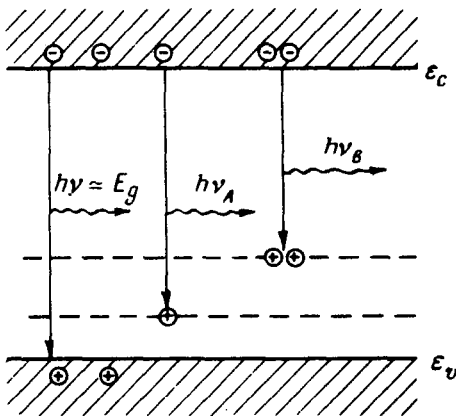


FIG. 3. Proposed scheme of radiative transitions in PbTe–SnTe–CdTe.

magnitude smaller than for the undoped material. When layers with this indium concentration were excited by a YAG laser, a new emission line (Fig. 1b) appeared in the photoluminescence spectra on the short-wavelength side, at an energy higher than the band gap E_g of an undoped layer. For indium concentrations in the transition region $(1-5) \times 10^{18} \text{ cm}^{-3}$, we observed radiation at energies between 0.13 and 0.16 eV in several of the samples. For higher indium concentrations only a line at 0.2 eV was observed. As the temperature was raised, the 0.2 eV line was shifted to shorter wavelengths (by 20–22 meV at 77 K). This line was observed, as a rule, at high (10^5 – 10^6 W/cm^2) levels of excitation. A possible explanation for the short-wavelength radiation is that it is due to transitions from resonant levels in the band which do not necessarily belong to indium. The indium only forms effective centers for nonradiative band-to-band transitions.

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