Luminescence in semiconductor-ferroelectric $Sn_2P_2Se_6$ crystals

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Received: 10.11.2007

Abstract

Luminescence spectra of $Sn_2P_2Se_6$ crystals are investigated in the temperature range of 8 – 67 *K*. On the basis of analysis of the obtained data we show that the broad emission band with the maximum at about 600 nm (for the temperature *T*=8.6 *K*) can be assigned to the band-to-band electron-hole recombination, whereas the broad emission bands peaked near 785 nm (*T*=8.6 *K*) and 1025 nm (*T*=44 *K*) can be assigned to electron-hole recombination from the levels of defects, which are localized within the bandgap. Based on the referenced data, possible types of the recombination defect centres in $Sn_2P_2Se_6$ crystals are discussed.

Keywords: $Sn_2P_2Se_6$ crystals, semiconductors, photoluminescence, electron-hole recombination

PACS: 78.55-m, 78.66.Li, 71.35-y, 77.80-e, 64.70.Rh.

Introduction

$Sn_2P_2Se_6$ crystals belong to a large crystalline family of $Sn_{2y}Pb_{2(1-y)}P_2S_{6x}Se_{6(1-x)}$ feroelectrics-semiconductors (see, e.g., [1]). These compounds are transparent in the infrared range up to 8μm (sulphides) or even up to 12μm (selenides). The bandgap energy, and so the high-frequency edge of transparency for the $Sn_{2y}Pb_{2(1-y)}P_2S_{6x}Se_{6(1-x)}$ crystals can be changed by Sn-Pb and S-Se atomic substitutions [2]. The latter edge is near 0.53μm in sulphides and 0.69μm in selenides.

$Sn_2P_2S_6$ crystals are proper ferroelectrics, while $Sn_2P_2Se_6$ manifests also an intermediate incommensurate phase between the ferroelectric and paraelectric ones. The crystals of this family are interesting from the point of view of their good electrooptic [3,4], piezooptic, acoustooptic [5–8] and photorefractive [9,10] properties. Unfortunately, the experimental data available on their electronic properties are rather limited, though they could be fruitfully used for modelling electron spectra and could make a basis for

understanding the charge transfer mechanisms, the optical and nonlinear optical parameters.

In particular, very useful information may be potentially obtained from the luminescence spectra. The first photoluminescence data for the semiconductor-ferroelectric $Sn_2P_2Se_6$ crystals have been published in the work [11]. In the present paper we investigate and analyze the photoluminescence spectra of $Sn_2P_2Se_6$ in the temperature region of 8–67 K.

Experimental details

Nominally pure $Sn_2P_2Se_6$ crystals have been obtained with the Bridgman technique [12]. $Sn_2P_2Se_6$ crystal exists in the following three phases: paraelectric, incommensurate and ferroelectric. In their paraelectric phase (above T_c=193 K), $Sn_2P_2Se_6$ belongs to the point group of symmetry *2/m*. In the ferroelectric phase (i.e., below T_c=193 K), the crystal is characterized by the point group m. Between the paraelectric and ferroelectric phases, spatially modulated incommensurate phase exists in the region defined by the relation T_c=193 K < T <T_i=221 K [13]. The "lock-in" phase transition occurring at the temperature T_c is of a first order, whereas the transition from the paraelectric phase at T_i is of a second order [14]. $Sn_2P_2Se_6$ crystals represent semiconductors with relatively narrow bandgap ($E_g = 1.8$ eV at $T = 293$ K and $E_g = 1.9$ eV at $T = 4.2$ K) [2].

The samples for the luminescence measurements have been cut to the sizes of $\sim 5 \times 5 \times 5\,\text{mm}^3$ and then polished. The photoluminescence has been excited with Ar-ion laser ($\lambda_{exc} = 514.5$ nm) and detected in the spectral region of $500 - 1200$ nm at a number of temperatures in the $8 - 67$ K region. A grating spectrophotometer of MDR-3 type has been used, equipped with a cooled FEU-62 photomultiplier tube.

Results and discussion

The photoluminescence spectra of $Sn_2P_2Se_6$ detected in the spectral region of 500–1200 nm at different temperatures are presented in Fig. 1 (T = 8.6 – 40 K) and Fig. 2 (T = 44 – 67 K). All of these data refer to the ferroelectric phase since they are obtained below T_c. As seen from Fig. 1, the luminescence spectrum of $Sn_2P_2Se_6$ crystals measured at T = 8.6 consists of a broad band (the FWHM is equal to $\Delta\lambda_{1/2} \cong 100$ nm) with the pronounced maximum at $\lambda_{max} \cong 600$ nm and a broad band (the FWHM is $\Delta\lambda_{1/2} \cong 100$ nm), peaked at 780 nm (see Fig. 1, curve a). Both the peak position and the integral intensity of the high-energy emission band remain practically invariable under temperature increasing in the whole range under studies (see Fig. 1 and 2).

The peak position of the low-energy emission band ($\lambda_{max} \cong 780$ nm at $T = 8.6$ K) also does not change, whereas its intensity decreases drastically with increasing temperature (see Fig. 1). As a result, the emission band with $\lambda_{max} \cong 780$ nm is difficult to observe at $T = 56$ K (Fig. 2, curve c). The other low-energy emission band ($\lambda_{max} \cong 1025$ nm at

$T = 44$ K – see Fig. 2) demonstrates similar temperature dependence (Fig. 1). In particular, the peak intensity is strongly reduced with increasing temperature and the band is hardly noticeable at $T = 67$ K (Fig. 2). It should be noted that the linewidths of the high-energy and low-energy photoluminescence bands are characterized by homogeneous broadening during the temperature increase from 8 to 67 K (see Fig. 1 and 2).

In the work [11] it has been suggested that the broad emission band (the FWHM $\Delta\lambda_{1/2} \cong 100$ nm) observed at $T = 2$ K and peaked near 765 nm refers to exciton

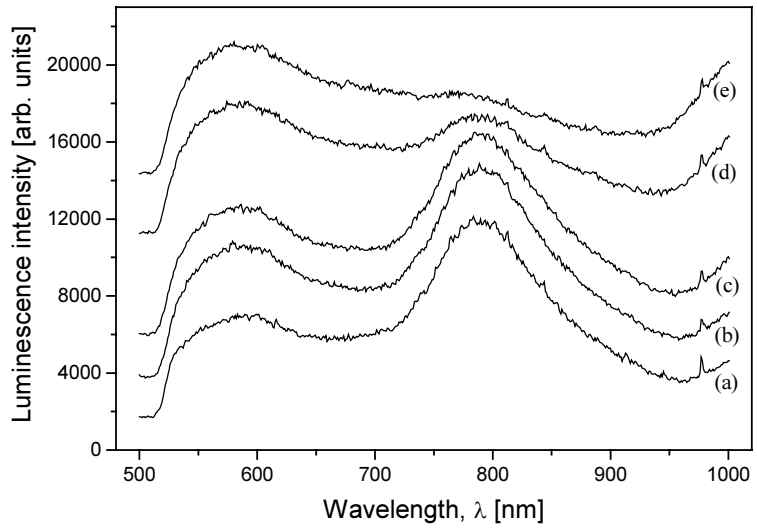

Fig. 1. Luminescence spectra of $Sn_2P_2Se_6$ crystals excited with the Ar-ion laser (λ_{exc}=514.5 nm) and detected at the temperatures 8.6 (a), 9.1 (b), 9.5 (c), 22 (d) and 40 K (e).

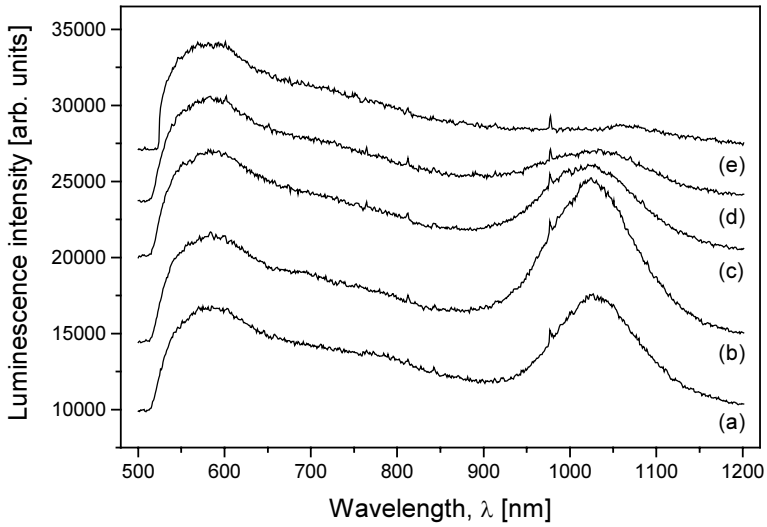

Fig. 2. Luminescence spectra of $Sn_2P_2Se_6$ crystals excited with Ar-ion laser (λ_{exc}=514.5 nm) and detected at the temperatures 44 (a), 50 (b), 56 (c), 62 (d) and 67 K (e).

luminescence, and so the shape and width of that band are presumably related to excitons confined by inhomogeneous local crystal field. On the basis of the experimental results and the referenced data on the photoluminescence of isostructural $Sn_2P_2S_6$ crystals [15–18], the authors of the mentioned paper have proposed the model and mechanisms of photoluminescence in $Sn_2P_2Se_6$ crystals.

Several studies on the photoluminescence of $Sn_2P_2S_6$ crystals have been published earlier (see [15–18]). In particular, it has been revealed that the luminescence spectrum of $Sn_2P_2S_6$ ($E_g \cong 2.4$ eV) consists of the two broad bands peaked at 1.7 and 2.1 eV, which are caused by optical transitions with participation of defect levels [15]. It has been noted in the mentioned work that the temperature increase from 4.5 to 40 K leads to strong decrease in the high-energy (2.1 eV) band intensity. Nonetheless, there is still no explanation of nature of the observed emission bands and their temperature dependences. Red and near-infrared photoluminescence bands in the undoped $Sn_2P_2S_6$ crystals have been observed in the study [16] at low temperatures under optical excitation (the excitation wavelength $\lambda < 710$ nm).

The emission and luminescence excitation spectra of nominally pure $Sn_2P_2S_6$ crystals have been investigated in [17] for the wide temperature ($12-360$ K) and spectral ($260-1200$ nm) ranges. The results obtained in [17] have been interpreted so that at least three photoluminescence bands (peaking near 1.28, 1.46 and 1.72 eV) peculiar for $Sn_2P_2S_6$ crystals are associated with sulphur vacancies. This is because the line intensities increase after heat treatment of $Sn_2P_2S_6$ crystals in vacuum, which should increase concentration of internal structure defects (i.e., vacancies). In [17] it has been suggested that the sulphur vacancies might probably create donor energy levels within the bandgap of $Sn_2P_2S_6$. Then the free electrons generated by the band-to-band illumination can be captured in the conduction band, while the free holes created in the valence band are captured on acceptor levels of different types. Thus, according to [17], the photoluminescence bands in $Sn_2P_2S_6$ crystals could be associated with the radiative recombination of donor-acceptor type, which is typical for semiconductors [19].

Another model of the recombination luminescence centres in $Sn_2P_2S_6$ crystals has been proposed in [18]. In this work the emission spectra, including time-resolved ones, have been registered at 4.5 K under the nitrogen (N_2) laser excitation ($\lambda_{exc} = 337.1$ nm). Taking into account the energy structure of $Sn_2P_2S_6$ crystals [20] and the thermoluminescence data [15], the authors [18] have assigned complex emission bands in the $2.1-3.5$ eV spectral region to electron-hole recombination among different conduction sub-bands and the top of the valence band. This assumption correlates with the regularities observed for the photodiffusion and photoconductivity spectra of $Sn_2P_2S_6$ crystals investigated in the work [18]. The processes of the electron-hole recombination in $Sn_2P_2S_6$ are very fast (nanosecond time region), because no significant difference is found between the stationary and time-resolved (with the delay time equal to 3.0 ns) luminescence spectra [18].

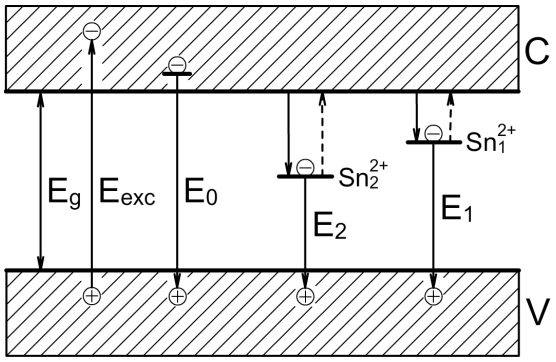

Fig. 3. Schematic representation of electron-hole recombination processes leading to emission in the semiconductor $Sn_2P_2Se_6$ crystals under photoexcitation with Ar-ion laser ($\lambda_{exc} = 514.5$ nm).

According to the results obtained in this work and the literature data on the photoluminescence in $Sn_2P_2S_6$ crystals considered above, we can put forward the recombination mechanism of the photoluminescence in $Sn_2P_2Se_6$ crystals. It is presented schematically in Fig. 3. The Ar-laser excitation ($E_{exc} \cong 2.41$ eV) leads to the electron transitions from the valence band to the conduction one (at low temperatures we have $E_g \cong 1.85$ eV). Thus, the complex broad high-energy emission band peaked near 600 nm ($E_0 \cong 2.1$ eV) could be assigned to the band-to-band electron-hole recombination (Fig. 3). Weak dependence on temperature of the high-energy emission band position correlates well with the temperature variation of the bandgap [2].

The low-energy emission bands, which are peaked at 780 nm ($E_1 \cong 1.6$ eV) and 1025 nm ($E_2 \cong 1.2$ eV), should be related to electron-hole recombination from the two levels of defects (Fig. 3). One can suppose that, most likely, the point defects in $Sn_2P_2Se_6$ crystals are mercury-like Sn^{2+} ions, as interpreted in the previous publications referred above. According to [18], the energy levels of Sn^{2+} are localized within the bandgap of $Sn_2P_2S_6$ ($E_1 = 1.85$ eV and $E_2 = 2.12$ eV), their positions being slightly dependent on temperature. Therefore, the photoluminescence bands peaked at 2.1 and 1.7 eV, which have been observed in $Sn_2P_2S_6$ crystals [15], can be related to recombination of electrons from Sn^{2+} levels with holes in the valence band. In our opinion, the low-energy luminescence bands taking place in $Sn_2P_2Se_6$ crystals have similar nature and mechanisms. Here the bandgap is narrower and the energies of the luminescence transitions smaller ($E_1 \cong 1.2$ eV and $E_2 \cong 1.6$ eV), when compared with the corresponding parameters observed in the case of $Sn_2P_2S_6$ crystals ($E_1 \cong 1.7$ eV and $E_2 \cong 2.1$ eV). Temperature dependence of the low-energy emission band intensity, associated with thermal decay of photoluminescence from the defect Sn^{2+} levels, can be explained on the basis of temperature-dependent generation-recombination processes occurring in semiconductors [19].

Detailed investigations of the photoluminescence spectra and decay kinetics of the crystal series $Sn_{2y}Pb_{2(1-y)}P_2S_{6x}Se_{6(1-x)}$ for a wide temperature range are now in progress.

Conclusions

Basing on the results obtained by us and the analysis of the literature data, the nature and specific mechanisms of the photoluminescence occurring in the ferroelectric phase of $Sn_2P_2S_6$ crystals are proposed. In particular, we show the following:

(1) Three broad photoluminescence bands peaked near 600 nm (2.1 eV), 780 nm (1.6 eV) and 1025 nm (1.2 eV) are observed under Ar-ion laser excitation at low temperatures (T < 40 K).

(2) The high-energy luminescence band ($E_0 \cong 2.1$ eV) with temperature-independent intensity is assigned to the band-to-band electron-hole recombination.

(3) The low-energy photoluminescence bands peaked at $E_1 \cong 1.2$ eV and $E_2 \cong 1.6$ eV are assigned to electron-hole recombination from the defect levels localized in the bandgap. Strong decrease in the intensity of low-energy emission bands with increasing temperature in the region of $8-87$ K should be explained by temperature-dependent generation-recombination processes taking place in the conditions of photoexcitation of semiconductors.

(4) The most probable defects in $Sn_2P_2Se_6$ crystals are mercury-like Sn^{2+} ions, with their energy levels localized in the bandgap. They take part in the generation-recombination processes under photoexcitation and form the low-energy luminescence bands peaked near 1.2 and 1.6 eV. This assumption needs further confirmation by direct studies of electron structure of the point defects.

Acknowledgements

The authors are grateful to the State Foundation of Fundamental Researches of Ukraine (Project No Ф25/552-2007) for financial support of this work.

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