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Optical and photoelectric spectroscopy of photorefractive $\text{Sn}_2\text{P}_2\text{S}_6$ crystals

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Abstract

Low-temperature studies of the absorption, photoluminescence, photodiffusion and photoconductivity spectra of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals were carried out in the wide spectral range 0.8–3.5 eV. The position of defect energy levels relative to the crystal energy bands has been determined. It was shown that the photoionization transitions from the valence band to the level with the energy $E_v + 1.35$ eV are caused by the presence of the hole metastable state. In the optical and photoelectric spectra several bands were revealed with energy greater than the band gap of the crystal ($E_g = 2.5$ eV). It was established that these bands are caused by the optical transitions between the valence band and upper conduction bands. It was shown that the electron–hole recombination, caused by the band-to-band transitions with the participation of the upper conduction subbands, is fast and corresponds to the nanosecond region. The combined scheme of the defect energy level and the band-to-band electronic phototransitions in $\text{Sn}_2\text{P}_2\text{S}_6$ crystals was constructed. A mechanism for the photorefractive effect in these crystals is proposed.

1. Introduction

$\text{Sn}_2\text{P}_2\text{S}_6$ crystals are ionic–covalent compounds [1–3]. These crystals attract special attention, since they are considered promising photorefractive materials. They combine ferroelectric and semiconductor properties, which makes it possible to obtain a photorefractive gain factor of $\Phi \approx 30 \text{ cm}^{-1}$ and a response time of about 10^{-3} s. The spectral range of the photosensitivity of such crystals spreads from 0.5 to $1.32 \mu\text{m}$ [5]. However, the mechanism of the photorefractive effect and the photoinduced changes in $\text{Sn}_2\text{P}_2\text{S}_6$ crystals are still not very clear and require additional studies. Such studies would help one optimize the photorefractive properties of

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these crystals and would contribute to their applications. At the present time, the studies of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals have mainly been devoted to the phase transitions, the phonon spectra and the peculiarities of photorefractive properties of such crystals depending on the technology of their growth [2, 5–7]. However, the studies of the nature of defect states as well as the position of their energy levels relative to the crystal energy band are at the first stage of understanding. Recently several papers have been published [8–11] which are devoted to studies of electronic structure of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals. It was shown [4] that the energy band spectrum of $\text{Sn}_2\text{P}_2\text{S}_6$ crystal is characterized by poor curvature of both the bottom of the conduction band and the top of the valence band, which indicates relatively high effective masses of the charge carriers. Such crystals have p-type conductivity, which is determined by the Sn vacancies.

In this work, low-temperature studies of the optical (absorption and photoluminescence) and photoelectric (photoconductivity and photodiffusion current) properties of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals were carried out. The studies revealed the defect states and determined their nature as well as the positions of the defect energy levels relative to the crystal energy bands and the type of the photoionization transitions. The combined scheme of defect energy level and the band-to-band electronic phototransitions in $\text{Sn}_2\text{P}_2\text{S}_6$ crystals was constructed. The mechanism for the photorefractive effect in these crystals is presented.

2. Experimental procedures

The non-doped $\text{Sn}_2\text{P}_2\text{S}_6$ crystals were grown by a gas-transport reaction. The parallel-sided crystal samples were prepared by mechanical treatment and then polished. The absorption, photoconductivity and photodiffusion current spectra were measured using an MDR-23 monochromator and processed with a computer. The samples were mounted on the cold finger of a variable temperature liquid-nitrogen cryostat. The accuracy of the measurements and temperature stabilization by the UTREKS system was 0.01 K. In these measurements, the light beam incident on the crystal sample was modulated by a mechanical chopper and the signal was measured using a phase-sensitive lock-in detection system. The spectral resolution of the system was about 1 cm^{-1} .

The photoconduction and photodiffusion spectra were measured along the [010] crystal direction. The ring In–Ga–Sn paste electrodes were deposited on polished front and rear (010) faces of the crystals. These faces were set perpendicular to the direction of incident monochromatic light propagation. The photodiffusion current (PDC) spectra were measured using plane-parallel samples whose thickness d satisfied the condition $kd \gg 1$, i.e. the light was adsorbed on the natural cleaved faces of the crystals perpendicular to the direction of the light propagation, and their ohmic resistance was checked. The experimental scheme is shown in figure 1.

The PDC experiments were carried out using a quartz halogen lamp as the light source. The diameter of the beam spot was 10–12 mm and the light intensity incident on the crystal face depended on the light wavelength. The illumination was homogeneous all over the crystal sample face including the electrodes. The maximum of the light intensity ($I_{\text{max}} = 1.08 \text{ mW cm}^{-2}$) corresponds to the wavelength at 650 nm (1.91 eV). For the wavelengths $\lambda_1 = 1000 \text{ nm}$ (1.24 eV) and $\lambda_2 = 350 \text{ nm}$ (3.54 eV) the light intensity corresponds to 0.639 and 0.146 mW cm^{-2} , respectively. Due to the nonuniform depth distribution of excess minority carriers in the crystal, illumination of the samples produces a diffusion current perpendicular to the crystal surface (since the cross section of the incident light was uniform, this eliminated carrier diffusion perpendicular to the direction of the light propagation). As a result of the establishment of equilibrium in an isolated sample, a potential difference is created between the illuminated and dark surfaces of the crystal, which is responsible for the Dember

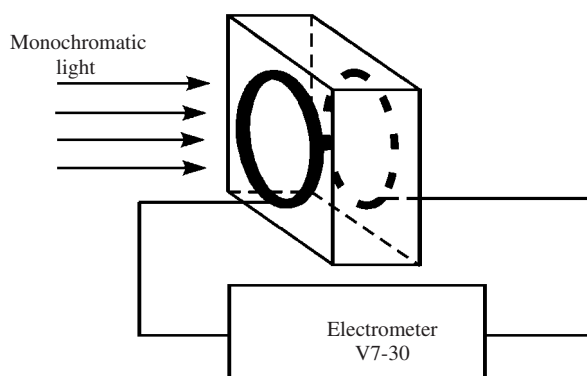


Figure 1. Experimental scheme for photodiffusion current measurement.

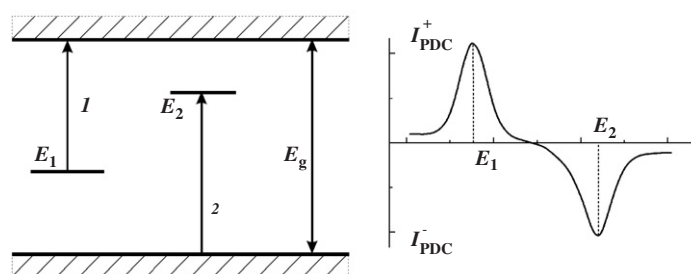


Figure 2. Diagram of the polarity of photoionization transitions in the measurement of the photodiffusion current.

photo-emf. In our measurements, the input resistance of the electrometer was much lower than the resistance of the samples, so in these experiments we measured a diffusion current close to the short circuit current. The direction of this current is determined by the direction of light propagation. The samples were exposed to monochromatic light. The polarity of the PDC was determined by the polarity of the charge observed at the front (illuminated) surface of the sample and was opposite to that of the excited carriers. The PDC spectra were normalized to the same number of incident photons. In the PDC spectra, the positive bands are caused by photoionization transitions of electrons from impurity or defect levels to the conduction band, while the negative bands are attributed to the excitation of valence-band electrons to discrete levels positioned in the crystal band gap (photoionization of holes from impurity levels to the valence band). A diagram of the polarity of photoionization transitions in the measurement of the photodiffusion current is shown in figure 2. Thus the PDC method has the advantage in comparison with the photoconduction (PC) measurements of photoionization transitions caused by the optical transitions between the defect (donor or acceptor) levels and the energy crystal bands. It makes it possible to determine not only the energy but also the type of phototransition (from defect levels to the conduction band or from the valence band to defect levels). Undoubtedly the measurements of both the PDC spectra and the PC spectra let us obtain more complete data regarding the photoionization transitions. Therefore in this paper the PDC and PC measurements are used.

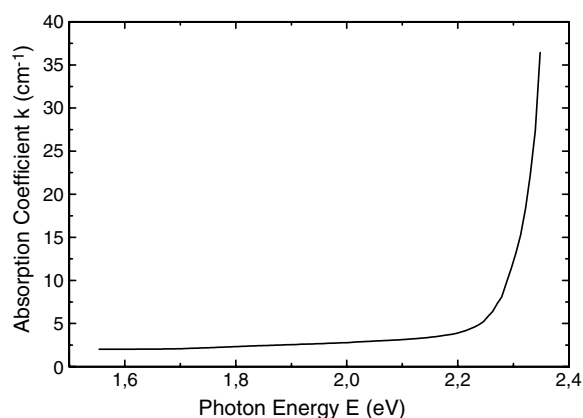


Figure 3. Absorption spectrum of $\text{Sn}_2\text{P}_2\text{S}_6$ at 295 K.

3. Experimental results and discussion

In figure 3 the absorption spectrum of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals is presented at 293 K. It shows that the absorption edge (for an absorption coefficient equal to 35 cm^{-1}) is positioned at an energy about 2.35 eV and the absorption of the crystal in the transparent spectral range is insignificant ($\leq 3 \text{ cm}^{-1}$). In figure 3 the absorption spectrum of the crystal is shown for the energy range from 1.55 to 2.35 eV. It should be noted that the absorption measurements of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals were carried out in a wider spectral range up to $\lambda = 1.8 \mu\text{m}$ ($\approx 0.69 \text{ eV}$). For energies smaller than 1.55 eV the absorption decreases (the absorption coefficient $k \approx 2 \text{ cm}^{-1}$ at the energy 0.7 eV) very smoothly. For energies greater than 2.35 eV, the absorption coefficient of $\text{Sn}_2\text{P}_2\text{S}_6$ crystal is strongly increasing. It is known that for the band-to-band transitions the value of k is $\approx 10^5 \text{ cm}^{-1}$. In our case the experimental equipment let us measure an absorption coefficient less than 40 cm^{-1} . The absorption spectrum of $\text{Sn}_2\text{P}_2\text{S}_6$ crystal in the spectral range from 1.6 to 2.2 eV indicates the possibility of the presence of optical photoionization transitions. In order to study photoionization transitions between the acceptor/donor centres and the energy bands of the crystal, and to determine the energies and types of the phototransitions, we used the measurements of the PDC and PC spectra of the investigated crystals. These measurements let us obtain more complete data regarding the photoionization transitions and enabled us to distinguish PDC peaks from troughs.

In figure 4 the PDC spectrum of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals at 78 K is shown. It should be noted that the negative PDC spectrum located in the spectral range 1.2–3.7 eV is caused by the photoionization of electrons from the valence band to the defect energy levels, which are positioned in the band gap. There are several PDC bands of negative polarity at the energies 1.35, 1.85, 2.12, 2.55 and 3.45 eV, indicated by the arrows in figure 4. It is also possible that positive PDC bands of small intensity can be present in the spectral range about 1.0 eV. The inflection shown on the low-energy edge of the 2.27 eV PDC band may be caused by the transitions to one of the conduction subbands, since the calculations of the band structure of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals indicate [10] that two conduction subbands have very close energies. Another mechanism for the appearance of a PDC band at 2.27 eV can be caused by the optical transitions from the valence band to the donor level (it is possible that this PDC band may be caused by the optical transitions from the acceptor levels to the conduction band) with the energy $\approx E_c - 0.29 \text{ eV}$. The negative PDC band at 3.45 eV is caused by the band-to-band transitions between the valence band and one of the conduction subbands [10].

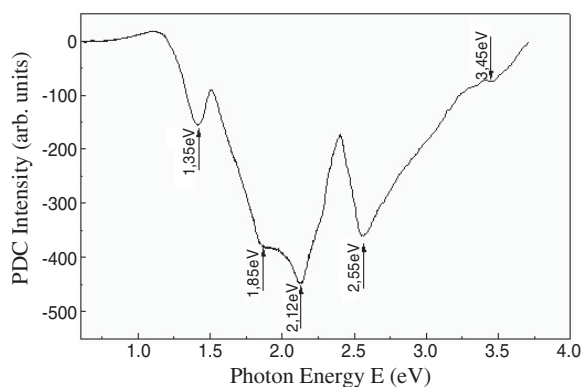


Figure 4. Photodiffusion current spectrum of $\text{Sn}_2\text{P}_2\text{S}_6$ at 78 K.

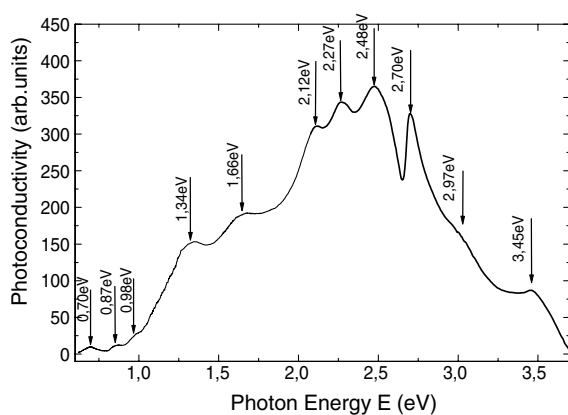


Figure 5. Photoconductivity spectrum of $\text{Sn}_2\text{P}_2\text{S}_6$ at 78 K.

It should be noted that the relative intensity of the PDC bands strongly depends on the method of the preparing of samples. When the crystal sample is heated above the ferroelectric phase transition temperature (≥ 337 K) and then cooled in the dark in short circuit conditions, the 2.55 eV band is the most intensive in the spectrum. The preliminary illumination of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals by light with the energy 2.60 eV produces a redistribution of intensity between different PDC bands. In this case, the intensity of the PDC bands at 1.85, 2.12 and 2.27 eV is essentially increased and the 2.55 eV band is strongly decreased. The heating of the crystal up to ≥ 337 K and the cooling in the dark leads to the reconstruction of the primary spectrum.

The measurements of the PC spectrum of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals let us determine both the energies of the photoionization transitions and the PDC bands of positive polarity in the region about 1.0 eV (shown as a wide band in the PDC spectrum) with higher precision. In figure 5 the PC spectrum is presented. As can be seen, the PC bands at 0.70, 0.87, 0.98, 1.34, 1.66, 2.12, 2.27, 2.48, 2.70, 2.97 and 3.45 eV appear in the spectrum. It should be noted that most of the PC bands with energy higher than 1.00 eV appear in the PDC spectrum too. Thus the PDC bands at 1.35, 2.12, 2.27, 2.55 and 3.45 eV correspond to the PC bands at 1.34, 2.12, 2.27, 2.48 and 3.45 eV, respectively. Three PC bands are located in the low-energy region at 0.70, 0.87 and 0.98 eV. The PDC bands at 2.70 and 3.00 eV are shown in figure 4 as a wide inflection.

It should be noted that the positive PDC band in the 0.8–1.2 eV range has been detected earlier. It was possible to observe the structure of this band in the PC spectrum because this spectrum was measured with better spectral resolution ratio since the signal intensity of the PC spectrum was stronger than that of the PDC spectrum. Therefore in fact we carried out the measurement of the PC spectrum with the better spectral resolution. The intensity of the monochromatic light was the same for both measurements. We think that the PC bands at 0.70, 0.87 and 0.98 eV correspond to the optical transitions from deep defect levels positioned in the band gap of $\text{Sn}_2\text{P}_2\text{S}_6$ crystal to the conduction band.

The appearance of the negative PDC band at 1.35 eV is correlated with the photo-EPR data obtained in [10]. In that research it was reported that holes are generated in $\text{Sn}_2\text{P}_2\text{S}_6$ crystals when excited by light with an energy of 1.40 eV. The holes are trapped by the Sn^{2+} ions. In this case the polaron state can appear in the $\text{Sn}_2\text{P}_2\text{S}_6$ crystal [12], i.e. the holes are trapped by the metastable states positioned in the band gap of the crystal. The results of the studies of PDC and PC spectra indicate that the metastable state corresponds to the energy level at $E_v + 1.35$ eV. It should be noted that illumination of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals by light with an energy of 2.0 eV leads to the disappearance of Sn^{3+} ions in the photo-EPR spectrum. In our opinion, it may be caused by the photoionization transitions from the valence band to the levels of Sn^{3+} ions and the formation of Sn^{2+} ions. Since for the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals there are two nonequivalent positions of Sn^{2+} ions, then it is obvious that the optical transitions at 1.85 and 2.12 eV can be caused by the acceptor photoionization of such levels. The PDC and PC bands at 2.27 eV are possibly caused by the optical transitions from the valence band to the level with the energy $E_c - 0.28$ eV, which is the trap for electrons. This coincides with the data for the thermoluminescence measurement of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals [13].

The photoluminescence (PL) spectra including a time-resolved spectrum of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals were measured at 4.5 K. A nitrogen laser was used for excitation of the spectra. Figure 6 presents PL spectra of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals in the range 2.1–3.5 eV at 4.5 K. It should be noted that the investigation of the PL spectra of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals under the excitation of a Hg lamp was carried out earlier [13] in the spectral range 1.48–2.07 eV, i.e. at energies smaller than the band gap of $\text{Sn}_2\text{P}_2\text{S}_6$. Two wide PL bands at 1.8 and 2.1 eV were revealed [13], which with no doubts are caused by the optical transitions with the participation of $\text{Sn}_2\text{P}_2\text{S}_6$ defect levels. It was noted that the increasing of the temperature from 4.5 to 40 K leads to the strong decreasing of the high-energy PL band intensity. In this work there is no explanation regarding the nature of PL bands and their temperature dependence. The thermoluminescence spectrum of $\text{Sn}_2\text{P}_2\text{S}_6$ [13] indicates the presence of carrier traps with energies $E_c - 0.041$ eV and $E_c - 0.088$ eV. The calculation of the energy bands of $\text{Sn}_2\text{P}_2\text{S}_6$ crystal, presented in [10], indicates the presence of five conduction subbands positioned above the lower conduction subband in the energy region of 1.2 eV. Taking into account the energy structure of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals, we think that the above-mentioned PL bands are caused by the electron–hole recombination between several conduction subbands from one hand and the top of valence band from the other hand, i.e. they correspond to the band-to-band transitions. This assumption correlates with the results of the PDC and PC spectra where the bands at 2.70, 3.00 and 3.45 eV are shown. It should be noted that the band at 3.00 eV is broadened and appears as a kink. Such a shape does not exclude the presence of another band at 2.82 eV. As can be seen, there are no significant differences between the stationary and time-resolved PL spectra (the delay time equals 3.0 ns). This indicates that the processes of electron–hole recombination in the spectral region above 2.3 eV are fast and take place in the nanosecond time region.

Figure 7 presents a combined scheme of defect energy level and band-to-band electronic phototransitions in $\text{Sn}_2\text{P}_2\text{S}_6$ crystals. The obtained results indicate that these crystals contain Sn^{2+} and Sn^{3+} states and metastable ($\text{Sn}^{2+} + \text{h}$) polaron states. These states are situated in two

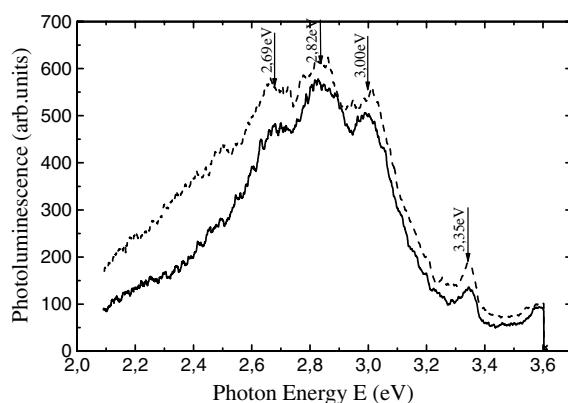


Figure 6. Stationary (solid line) and time-resolved (dotted line) photoluminescence spectra of $\text{Sn}_2\text{P}_2\text{S}_6$ at 4.5 K.

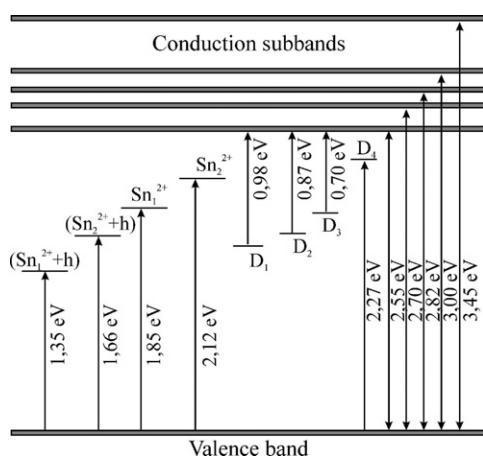


Figure 7. Scheme of the defect energy levels and electronic phototransitions of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals.

nonequivalent positions. Besides, there are some (D_1 – D_4) donor states. In this case, the positive charges of the Sn^{3+} ions are clearly compensated by the presence of these donor states as well as the shallow donor states revealed in the thermoluminescence. The donor concentration in the dark should correspond to that of the triply charged Sn ions.

According to the presented results, we propose the following mechanism for the photorefractive effect in these crystals. It is known that the photorefractive effect is a phenomenon in which the local index of refraction is changed by the spatial variation of the light intensity. Nonlinear optical processes including two-wave mixing are typical characteristics of the photorefractive effect that can be observed in crystals possessing both electrooptic and photoconductive properties. $\text{Sn}_2\text{P}_2\text{S}_6$ crystals belong to such type of semiconductors. It should be noted that a refractive grating is created in the photorefractive crystal as a result of the illumination of the crystal sample surface by two coherent light beams. In this case an interference pattern is produced on the crystal surface. When $\text{Sn}_2\text{P}_2\text{S}_6$ crystals are excited by He–Ne laser light ($h\nu = 1.96$ eV), a photorefractive effect may occur as a result of photoionization of Sn^{3+} ions with energy 1.85 and 2.12 eV. It should be noted that

when a $\text{Sn}_2\text{P}_2\text{S}_6$ crystal is excited by He–Ne laser light at $T = 300$ K, the Sn_2^{3+} centres with the photoionization energy 2.12 eV may undergo photoionization as a result of optical transitions involving the absorption of two longitudinal optical phonons with energy 76 meV (607 cm^{-1}) [7]. The photoionization transitions with the energies 1.85 and 2.12 eV correspond to the phototransitions of the electrons from the valence band to the Sn^{3+} states. In this case, Sn^{2+} ions are formed and free holes are created in the valence band. It should be noted that EPR measurement of $\text{Sn}_2\text{P}_2\text{S}_6$ [14] supports the identification of holes as the dominating charge carriers in this crystal. These carriers migrate by diffusion or drift from the regions of high illumination to the regions of low illumination and then are trapped by the Sn^{2+} centres to form the positive charged Sn^{3+} centres. Thus, in the regions of the crystal corresponding to the maximum of the interference pattern, the concentration of Sn^{3+} centres is lower than that required to compensate for the negatively charged donor centres. In other regions of the crystal some distance from the maximum of the interference pattern, there is an excess of Sn^{3+} centres as a result of trapping of holes by Sn^{2+} centres. Consequently, the trapped charges are distributed in space according to the light intensity distribution of the interference pattern. The excess of uncompensated donor states near the interference pattern maximum and the excess of Sn^{3+} centres in the other parts of the crystal lead to the formation of a periodic space charge field, which modulates the refractive index and thus produces the photorefractive effect [15].

It should be noted that the phase of the space-charge field is shifted in comparison with the interference pattern. This phase shift can have values between 0 and π depending on the transport mechanism of the charge carriers during the formation of the space-charge field [15]. The recording of the grating in the pure diffusion regime leads to a phase shift equal to $\pi/2$. Thus in photorefractive crystals the interference of two coherent beams creates a refractive-index grating corresponding to the interference pattern but with a shifted spatial phase. This phase shift leads to an energy transfer between the beams, i.e. the signal beam is amplified at the expense of the pump beam. This process is called photorefractive two-beam coupling.

In our opinion, the proposed scheme of the defect energy level in $\text{Sn}_2\text{P}_2\text{S}_6$ crystals lets us understand how the PDC spectra depend on the method of the sample preparation. It should be noted that $\text{Sn}_2\text{P}_2\text{S}_6$ crystals are characterized by the presence of a domain structure in the ferroelectric state. Therefore, in this case, the localization of the carriers near the domain walls [16] is possible. When the crystal sample is heated above the ferroelectric phase transition temperature (≥ 337 K), the domain structure is damaged. In this case the localized carriers are free. Since the crystal sample is in the dark and in the regime of short circuit the charged carriers can migrate into the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals. The transition of $\text{Sn}_2\text{P}_2\text{S}_6$ into the ferroelectric state lets the charge carriers diffuse and drift in the depolarizing field of the domain structure [16]. The redistribution of intensity between the different PDC bands and, in particular, the decrease of the intensity of the bands at 1.85 and 2.12 eV may be caused by the decreasing of concentration of Sn^{3+} ions as a result of the trapping of free electrons by these ions. In this case, the 2.56 eV band that corresponds to the band-to-band transitions will be most intensive in the spectrum.

The preliminary illumination of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals using light with energy 2.56 eV leads to the photogeneration of the free charge carriers both in the valence and in the conduction bands. The intensity of the PDC bands at 1.85 and 2.12 eV is essentially increased, which may be caused by the increasing of the concentration of Sn^{3+} ions. Obviously the free holes are trapped by the Sn^{2+} centres which are recharged into the Sn^{3+} states. Besides, the free holes may be trapped near Sn^{2+} ions and hole polaron states created. Thus only a portion of free electrons is able to recombine with the free holes. The other electrons remain free in the conduction band. This leads to the increasing of dark conductivity. These results are in good agreement with the photoinduced changes of the dark conductivity. It was established that the

illumination of Sn₂P₂S₆ crystals by white light leads to the appearance of photoinduced dark conductivity [17]. In this case the resistance of the crystal sample is decreased. Besides, it was shown that this illumination of Sn₂P₂S₆ leads to an increase of the photorefractive gain by a factor of 6 [14]. In our opinion, this may be caused by the increasing of the effective trap density as a result of the increasing of the photoinduced Sn³⁺ ions [18].

4. Summary

Complex optical and photoelectric studies of Sn₂P₂S₆ crystals in the spectral region 0.8–3.5 eV were carried out. A detailed analysis of the spectral dependence of PDC and photoconductivity spectra let us determine some deep impurity levels in the band gap. It was shown that the level with energy $E_v + 1.35$ eV is caused by the metastable state. The appearance of other levels with the energies $E_v + 1.85$ eV and $E_v + 2.12$ eV are caused by the acceptor photoionization of Sn³⁺ ions located in two nonequivalent positions. It was shown that the PDC and photoconductivity bands at 0.70, 0.87 and 0.98 eV are caused by donor photoionization from the deep impurity levels to the conduction band. It was established that some PL, PDC and PC bands at energies greater than the band gap of Sn₂P₂S₆ crystals are obviously caused by the band-to-band transitions with the participation of the valence band and several upper conduction subbands. It was shown that the electron–hole recombination is fast and takes place in the nanosecond range. A combined scheme of defect energy level and band-to-band electronic phototransitions in Sn₂P₂S₆ crystals was constructed. The obtained results indicate that there are Sn²⁺, Sn³⁺ and metastable (Sn²⁺ + h) states in these crystals. They are situated in two nonequivalent positions. Besides, there are some (D₁–D₂) donor states. It was shown that the charge compensation for Sn₂P₂S₆ crystals is caused by the presence of triply charged Sn ions and some deep and shallow donor states. The micromechanism of the photorefractive effect based on the obtained results has been presented. The nature of the electronic processes responsible for the photoinduced changes of the photoelectric properties of the investigated crystals was established.

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