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Time-resolved photoluminescence of ZnSe and ZnSe:Te single crystals

This study examines the time-resolved photoluminescence spectra of zinc selenide (ZnSe) single crystals, both undoped and doped with the isovalent tellurium impurity, at 83 K, together with their steady-state photoluminescence spectra. The ZnSe crystals were excited using a nitrogen laser with a wavelength of 347 nm. In the steady-state photoluminescence spectra of undoped ZnSe, three emission bands were observed, with maxima at approximately 443, 458, and 610 nm. Time-resolved luminescence spectroscopy made it possible to resolve the 610 nm band into two components, with maxima near 580 and 640 nm. In the steady-state spectra of tellurium-doped ZnSe crystals, three emission bands were also detected, with maxima at approximately 450, 505, and 640 nm. Time-resolved photoluminescence spectra allowed the 505 nm band to be resolved into two components, with maxima near 485 and 510 nm. The intensity of the red emission band at 640 nm increases with increasing tellurium concentration. It is hypothesized that this red photoluminescence band is associated with an intracentric transition of an associative defect involving a zinc vacancy, an interstitial zinc atom, and a tellurium atom substituting for selenium. Considering the presence of an uncontrolled aluminium impurity in the crystals, an alternative interpretation is also possible: the 640 nm band may originate from an intracentric transition within a defect complex comprising a zinc vacancy, an aluminium atom substituting for zinc, and a tellurium atom substituting for selenium.

Keywords: isovalent impurity, complex of defects, bound exciton, intracentric transition, vacancy, substitution, afterglow time, emission band

Introduction

Zinc selenide (ZnSe) is known for a number of properties, such as a high probability of radiative recombination due to direct optical transitions, a high photoluminescence quantum yield, and high photosensitivity which make it attractive for optoelectronic applications. It is a semiconductor material with high transparency in the infrared region and excellent optical properties.

ZnSe is used in several key areas, one of the most important being infrared optics. Components fabricated from ZnSe include lenses, laser windows, protective optical elements, and focusing systems for CO₂ lasers. The material transmits radiation over a wide spectral range (approximately 0.5 to 20 μm), making it suitable for high-power infrared lasers and thermal imaging systems. ZnSe is also widely used in thermal imaging cameras, night vision devices, pyrometers, and infrared spectrometers.

The properties of ZnSe crystals that undergo technological processing and are used in optoelectronic devices strongly depend on the characteristics of the initial crystals, including their background impurity content and intrinsic defects. Defects present in the material can give rise to localized electronic states within the band gap of the semiconductor, which act as recombination centers. Recombination involving these centers may be either radiative or non-radiative.

Due to intense luminescence of zinc selenide in the visible spectral range, its radiative properties have long been the subject of extensive research. However, the interpretation of luminescence spectra of both self-activated and impurity-doped ZnSe remains highly controversial. Time-resolved luminescence spectroscopy makes it possible to distinguish individual emission bands within the overall spectral profile, each characterized by different decay times.

In [1], low temperature ($T = 4.2$ K) time-resolved photoluminescence spectra were studied for initial ZnSe crystals purified by zone sublimation, as well as for crystals annealed in liquid zinc and bismuth. In addition to the near band-edge emission lines, a broad green photoluminescence band with a maximum at

approximately 520 nm (2.38 eV) and a relatively long decay time (on the order of 1 μ s) was observed in the initial crystals. This band disappeared after annealing in liquid zinc and bismuth.

The aim of the present work is to clarify the nature of the centers responsible for ZnSe emissions in the 500–700 nm spectral region.

Experimental

To investigate photoluminescence spectra in the visible range, we prepared ZnSe single-crystal samples similar to those studied in [1]. These were large-block ZnSe single crystals of the sphalerite structure, grown from the melt under pressure without intentional doping. The crystals exhibited a dark resistivity on the order of $10^{12} \Omega \cdot \text{cm}$ and *n*-type conductivity with an electron concentration of approximately 10^7 cm^{-3} .

Plate-shaped samples with parallel faces and a thickness of 1–3 mm were obtained from these crystals by cleavage along the (110) plane.

In [2], secondary ion mass spectrometry (SIMS) revealed the presence of background impurities in similarly prepared ZnSe samples, including aluminum, manganese, iron, indium, chromium, and tellurium, with concentration on the order of 10^{17} cm^{-3} .

To clarify the nature of certain emission bands, additional samples doped with an isovalent tellurium impurity were also prepared.

A pulsed nitrogen laser (LGI-21) with a wavelength of 337 nm was used as the excitation source for photoluminescence. The laser operated with pulse duration of 10 ns, pulse energy of 30 μ J, and a repetition rate of 100 pulses per second. Photoluminescence spectra were recorded at a temperature of $T = 83 \text{ K}$.

The experimental setup for time-resolved photoluminescence spectroscopy allowed variation of the detection time window from 0.2 ns to 40 μ s, as well as shifting of this window by up to 100 ms relative to the excitation pulse.

Results and Discussion

Figure 1 shows the emissions spectrum of the initial ZnSe sample at a temperature of 83 K. The photoluminescence spectrum is dominated by a broad long-wavelength band with a maximum at approximately 610 nm (2.03 eV). In addition, emission bands with maxima at 443 nm (2.80 eV) and 458 nm (2.71 eV) are observed.

It is most likely that the band at 443 nm is associated with radiative recombination of free excitons [3], while the 458 nm band can be attributed to bound excitons [4].

Time-resolved luminescence spectroscopy of the same initial ZnSe crystals showed that, at delay times ranging from 0 to several hundred nanoseconds, the shape of the long wave-length band with a maximum near 610 nm changes. At a delay time of 500 ns, two distinct maxima appear in the spectrum at 580 nm (2.14 eV) and 640 nm (1.94 eV) (Fig. 2).

The orange emission band with a maximum at 580 nm is commonly attributed to donor-acceptor pair recombination involving deep acceptor states (such as zinc vacancies, interstitial zinc, and impurity centers) [5].

Given the presence of a background manganese impurity in the studied samples, it can also be suggested that the 580 nm band is related to an intracenter transition of manganese ions [6].

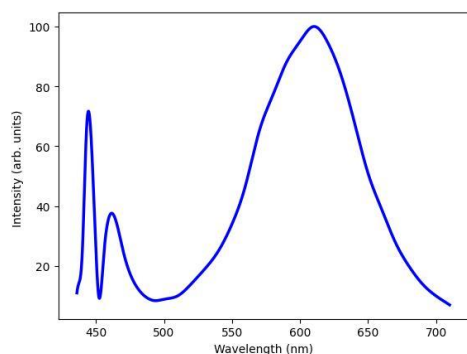


Figure 1. Photoluminescence spectrum of ZnSe with background impurities at $T = 83 \text{ K}$

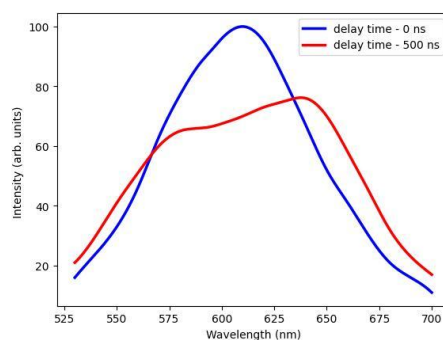


Figure 2. Red photoluminescence band of ZnSe at different delay times 0 ns (blue line) and 500 ns (red line)

The long-wavelength emission band with a maximum in the range of 615–645 nm is commonly described in the literature as non-elementary and is associated with complexes involving zinc vacancies and impurity atoms that give rise to both acceptor and donor levels [3, 7–9].

The authors of [10] proposed a structural model for the centre responsible for the luminescence band at 630 nm, suggesting a complex defect consisting of an isoelectronic substitution (such as selenium, oxygen, or tellurium) located in the vicinity of a zinc vacancy.

In [11], red emission in the 646–662 nm range is attributed to Frenkel-type defects of the form $\text{O} = \text{Cr}_i^{2+} + \text{V}_{\text{Zn}}$, where Cr^{2+} occupies an interstitial position at a chromium concentration of approximately $2 \times 10^{18} \text{ cm}^{-3}$.

It should be noted that the emission band near 640 nm observed in the present study is characterized by a relatively long decay time (on the order of several nanoseconds). A similar decay time was reported in [1], where it was also shown that the intensity of this band decreases after annealing the samples in liquid zinc and liquid bismuth. Such annealing processes are known to reduce the concentration of zinc vacancies.

We proposed that the luminescence band near 640 nm originates from an intracenter transition of a defect complex $(\text{V}_{\text{Zn}} - \text{Zn}_i - \text{TeSe})^-$ from an excited state to the ground state. To clarify the nature of this band, we investigated photoluminescence spectra of ZnSe crystals doped with an isovalent tellurium impurity.

Figure 3 shows the photoluminescence spectrum of ZnSe crystals at 83 K with tellurium concentrations of approximately 0.5 % and 1 %. Three emission bands with maxima at 450 nm, 505 nm, and 640 nm are observed in the spectra. With increasing tellurium concentration, the intensities of the 450 nm and 505 nm bands decrease, while the intensity of the 640 nm band increases.

Time-resolved photoluminescence measurements made it possible to resolve the 505 nm band into two components with maxima at approximately 485 nm and 510 nm (Fig. 4). Thus, four emission bands — 450 nm, 485 nm, 510 nm, and 640 nm were identified in Te-doped ZnSe crystals.

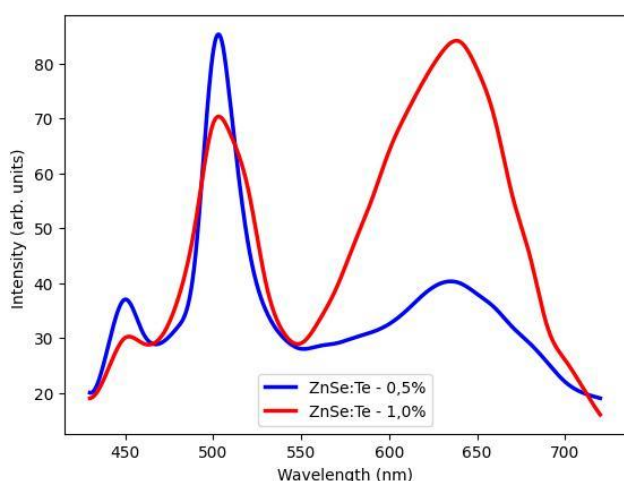


Figure 3. Photoluminescence spectra of ZnSe:Te crystals with tellurium concentrations of 0.5 % (blue line) and 1.0 % (red line)

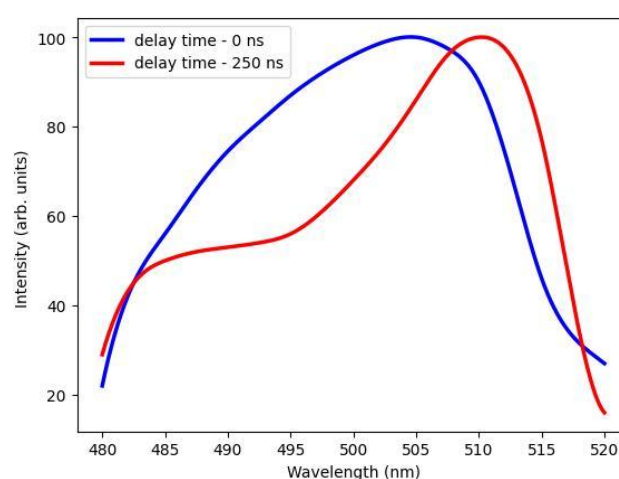


Figure 4. 505 nm emission band of ZnSe:Te recorded at different delay times: 0 ns (blue line), 250 ns (red line)

The increase in the intensity of the 640 nm band with increasing tellurium concentration suggests that tellurium is involved in the formation of this emission band. The relatively long decay time, which coincides with that of the 640 nm band observed in nominally undoped ZnSe crystals, supports the identification of these bands as originating from the same center.

As shown in [1], the intensity of the 640 nm band decreases after annealing in liquid zinc and liquid bismuth, conditions under which zinc vacancies are expected to be reduced. Upon increasing the measurement temperature from 83 K to 300 K, the spectral position of the 640 nm band remains unchanged. Taken together, these observations provide strong support for assigning this band to an intracenter transition within a complex vacancy-impurity defect.

Since the as-grown ZnSe crystals contain background aluminum impurities, it is reasonable to assume that aluminum may act as a donor in the complex centre, replacing the zinc vacancy; in this case, the defect can be written as $(\text{V}_{\text{Zn}} - \text{Al}_{\text{Zn}} - \text{TeSe})^-$ instead of $(\text{V}_{\text{Zn}} - \text{Zn}_i - \text{TeSe})^-$.

The emission band with a maximum at 450 nm is most likely a red-shifted counterpart of the 443 nm band previously observed in nominally undoped crystals, with the shift arising from the increased tellurium concentration.

The emission bands with maxima at 485 nm and 510 nm are most plausibly attributed to recombination via a donor level and an acceptor level associated with a zinc vacancy [3, 8, 12].

Conclusion

Time-resolved photoluminescence measurements of ZnSe single crystals at $T = 83$ K revealed that the broad emission band centered at 610 nm contains two distinct components with maxima at 580 nm and 640 nm. In addition, the 505 nm emission band observed in Te-doped ZnSe crystals was resolved into two bands at 485 nm and 510 nm.

Based on the obtained results and analysis of the available literature data, it is proposed that the 640 nm (1.94 eV) emission band originates from intracenter transitions and is associated with the presence of an isovalent tellurium impurity in ZnSe crystals, incorporated into a complex defect of the type $(V_{Zn}-Al_{Zn}-Te_{Se})^-$ or $(V_{Zn}-Zn_{Te}-Te_{Se})^-$.

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ZnSe және ZnSe:Te монокристалдарының уақыт бойынша ажыратылған фотолюминесценциясы

Жұмыста арнайы легирленбеген және теллурдың изовалентті қоспасымен легирленген мырыш селениді монокристалдарының $T = 83$ К температурасындағы уақыт бойынша ажыратылған фотолюминесценция спектрлері мен кәдімгі фотолюминесценция спектрлері қарастырылды. ZnSe кристалдарының сәулеленуі толқын ұзындығы 337 нм болатын азот лазерімен қоздырылды. Легирленбеген ZnSe кристалдарының кәдімгі фотолюминесценция спектрлерінде максимумдары шамамен 443 нм, 458 нм және 610 нм болатын үш сәулелену жолағы байқалды. Уақыт бойынша ажыратылған люминесценттік спектроскопия әдісі 610 нм жолағын максимумдары шамамен 580 нм және 640 нм болатын екі құрамдас жолаққа бөлуге мүмкіндік берді. Теллурмен легирленген мырыш селениді кристалдарының кәдімгі фотолюминесценция спектрлерінде де максимумдары шамамен 450 нм, 505 нм және 640 нм болатын үш сәулелену жолағы анықталды. Уақыт бойынша ажыратылған фотолюминесценция спектрлері 505 нм жолағынан максимумдары шамамен 485 нм және 510 нм болатын екі жолақты бөліп көрсетуге мүмкіндік берді. 640 нм аймағындағы қызыл сәулелену жолағының қарқындылығы теллур концентрациясының артуымен өсетіні анықталды. Бұл қызыл фотолюминесценция жолағы селен атомын алмастырған теллур атомының, мырыш вакансиясының және түйінаралық кеңістіктегі мырыш атомының қатысуымен түзілетін ассоциативті ақаудың ішкіорталықтық ауысуымен байланысты деген болжам ұсынылды. Кристалдарда бақыланбайтын алюминий қоспасының болуын ескере отырып, 640 нм жолағын мырыш вакансиясын, мырыш орнын басқан алюминий атомын және селен орнын басқан теллур атомын камтитын ақаулар кешеніндегі ішкіорталықтық ауысу ретінде түсіндіру де мүмкін.

Кілт сөздер: изовалентті қоспа, ақаулар кешені, байланысқан экситон, ішкіорталықтық ауысу, вакансия, орын басу, кейінгі жарқырау уақыты, сәулелену жолағы

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Разрешённая во времени фотолюминесценция монокристаллов ZnSe и ZnSe:Te

В работе рассмотрены спектры фотолюминесценции, разрешенные во времени, монокристаллов селенида цинка без специального легирования и легированных изовалентной примесью теллура при температуре $T = 83$ К и обычные спектры. Излучение кристаллов ZnSe возбуждалось азотным лазером с длиной волны 337 нм. На обычных спектрах фотолюминесценции нелегированных ZnSe наблюдались три полосы излучения с максимумами около 443 нм, 458 нм и 610 нм. Метод временной люминесцентной спектроскопии позволил из полосы 610 нм выделить две с максимумами около 580 нм и 640 нм. В обычных спектрах фотолюминесценции кристаллов селенида цинка, легированных теллуром, присутствовали три полосы излучения с максимумами около 450 нм, 505 нм и 640 нм. Разрешённые во времени спектры фотолюминесценции из полосы 505 нм выделили две с максимумами около 485 нм и 510 нм. Интенсивность красной полосы излучения 640 нм увеличивается с увеличением концентрации теллура. Выдвинута гипотеза, что красная полоса фотолюминесценции 640 нм обусловлена внутрицентровым переходом ассоциативного дефекта с участием вакансии цинка, цинка в междоузлии и теллура, замещающего селен. С учётом присутствия в кристаллах неконтролируемой примеси алюминия, также возможна интерпретация полосы 640 нм как внутрицентральной переход комплекса дефектов, включающего вакансию цинка, алюминий, замещающий цинк, и теллур, замещающий селен.

Ключевые слова: изовалентная примесь, комплекс дефектов, связанный экситон, внутрицентральной переход, вакансия, замещение, время послесвечения, полоса излучения

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