Faraday effect in $TlIn(S_{1-x}Se_x)_2$ solid solutions (x = 0, 0.02, 0.06, 0.10, 0.15 and 0.25)

[1] Adamenko D., [1] Krupych O., [1] Kostyrko M., [1]Vasylkiv Yu., [1,2] Gomonnai O., [2, 3] Gomonnai A. and [1] Vlokh R.

[1] Vlokh Institute of Physical Optics, 23 Dragomanov Street, 79005 Lviv, Ukraine, vlokh@ifo.lviv.ua
[2] Uzhhorod National University, 46 Pidhirna Street, 88000 Uzhhorod, Ukraine
[3] Institute of Electron Physics, Ukrainian National Academy of Sciences, 21 Universytetska Street, 88017 Uzhhorod, Ukraine

Received: 07.09.2020

Abstract. We have studied experimentally the Faraday effect in monoclinic $TlIn(S_{1-x}Se_x)_2$ solid solutions with selenium concentrations x changing in the range $0 \le x \le 0.25$. The Verdet constant V_F and the effective Faraday coefficient F'_{33} are determined at the light wavelength $\lambda = 632.8$ nm under normal conditions. We show that the both coefficients tend to increase when the Se concentration increases from 0 to 0.25. This behaviour is explained by dispersion of the Faraday coefficients and a shift of the absorption edge towards long-wavelength spectral range, which occurs with increasing amount of selenium.

Keywords: Faraday effect, Verdet constant, $TlIn(S_{1-x}Se_x)_2$ solid solutions

UDC: 537.632.4

1. Introduction

β-$TlInS_2$ and $TlInSe_2$ are halcogenides that belong to a $A^{III}B^{III}C^{IV}{}_2$ group of semiconductors, with A = Tl, B = Ga and In, and C = S, Se and Te [1]. $TlGaS_2$, $TlInS_2$ and $TlGaSe_2$ are monoclinic and reveal a layered structure [2–4], while tetragonal $TlGaTe_2$, $TlInTe_2$ and $TlInSe_2$ crystallize in a chain structure [5]. Under ambient conditions, $TlInS_2$ belongs to the monoclinic point symmetry group 2/*m* (the space group *C*2/*c* and *Z* = 16), with the two-fold symmetry axis being parallel to the crystallographic axis *c* [2]. The unit-cell parameters obtained from X-ray diffraction studies are equal to $a = 10.90$ Å, $b = 10.94$ Å, $c^* = 15.18$ Å and $\beta = 90.17$ deg [6]. The cleavage plane in $TlInS_2$ is perpendicular to the *c* axis, while a small difference between the lattice parameters *a* and *b* makes the unit cell of $TlInS_2$ close to tetragonal one [2]. At cooling, the crystal undergoes a phase transition into a ferroelectric phase through an incommensurate one [2, 7, 8]. The main peculiarity of the phase transitions in $TlInS_2$ is that different polytypes can coexist in a crystalline matrix [9, 10], which are characterized by different lattice parameters *c*. This parameter can be equal to $c = 2c^*$, $4c^*$, $8c^*$ and $16c^*$ for different polytypes, with $c^* = 15.18$ Å.

Studies of Raman scattering [11], infrared reflection spectra [12, 13], dielectric properties [14, 15], X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray spectroscopy [16] have earlier been reported for the mixed crystals of $TlIn(S_{1-x}Se_x)_2$ system. When the Se concentration x increases, the crystal structure changes from monoclinic (*C*2/*c*) to tetragonal (*I*4/*mcm*) at the x level approximately equal to 0.7–0.75 [11, 14]. Basing on the dielectric measurements, S–Se substitution in the $TlIn(S_{1-x}Se_x)_2$ crystals has been shown to result in decreasing phase-transition temperatures. We have arrived at the same conclusion using the optical anisotropy studies and the thermal expansion data derived with dilatometric methods [17, 18].

In the work [17], the Faraday rotation in the pure $TlInS_2$ crystal has been studied experimentally. The Verdet constant $V_F = (112.4\pm1.5)$ rad/(T×m) and the effective Faraday coefficient F'_{33} = 1.296±0.018 pm/A have been determined under normal conditions. This corresponds to the case when both the light beam and the magnetic field are directed along one of the optic axes. We have shown that, among magnetically non-ordered substances, $TlInS_2$ represents an efficient magneto-optic material.

Note that, since the angle between the optic axes in $TlIn(S_{1-x}Se_x)_2$ is quite small [18], these solid solutions are convenient for the studies of Faraday rotation in a longitudinal experimental geometry. The latter implies the geometry when the magnetic field vector is parallel to the wave vector of optical radiation and the both vectors are almost parallel to the *c* axis. The appropriate studies are the main goal of the present work.

2. Experimental procedures and results

At the normal conditions and the light wavelength $\lambda = 632.8$ nm, the plane containing the optic axes of all of the mixed $TlIn(S_{1-x}Se_x)_2$ crystals with $0 \le x \le 0.25$ coincides with the crystallographic plane *ca*, where the *c* axis represents the acute bisector of the angle 2Θ between the optic axes. We have measured the angle Θ between the optic axes and the *c* axis at $\lambda = 632.8$ nm for the $TlIn(S_{1-x}Se_x)_2$ solid solutions. This angle is equal to 1.3, 1.7, 1.4, 1.3, 1.5 and 0.9 deg respectively for the x = 0, 0.02, 0.06, 0.10, 0.15 and 0.25.

Suppose that the light wave propagates along one of the optic axes and the magnetic field is applied along the same direction. Then the Faraday effect manifests itself as a rotation of polarization plane of linearly polarized light. Under these conditions, the magnetically perturbed optical-frequency dielectric impermeability tensor components B_{jk} and the specific optical rotation angle $\Delta\rho_l$ are defined by the relations

$$B_{jk} = B^0_{jk} + ie_{jkl}F_{lm}H_m , \tag{1}$$

$$\Delta\rho_l = \frac{\pi n^3}{\lambda} F_{lm}H_m , \tag{2}$$

where B^0_{jk} implies the components of the impermeability tensor in the absence of external magnetic field H_m, e_{jkd} are the Levi–Civita symbols, n the refractive index for the light propagation direction, and F_{lm} the Faraday tensor components. For the case of point group 2/m, the latter tensor acquires the following form (in the coordinate system associated with the axes of Fresnel ellipsoid):

$$\mathbf{F} = \begin{bmatrix} F_{11} & F_{12} & 0 \\ F_{12} & F_{22} & 0 \\ 0 & 0 & F_{33} \end{bmatrix}. \tag{3}$$

When the light wave vector and the magnetic field are directed along the optic axis, which is tilted with respect to the *c* axis (in the crystallographic plane *ca*) by the angle Θ, the Faraday tensor given by Eq. (3) has to be rewritten in the coordinate system of which Z' axis is parallel to the optic axis:

$$\mathbf{F}' = \begin{bmatrix} F_{11}\cos^2\Theta + F_{33}\sin^2\Theta & F_{12}\cos\Theta & (F_{33}-F_{11})\sin\Theta\cos\Theta \\ F_{12}\cos\Theta & F_{22} & -F_{12}\sin\Theta \\ (F_{33}-F_{11})\sin\Theta\cos\Theta & -F_{12}\sin\Theta & (F_{33}\cos^2\Theta + F_{11}\sin^2\Theta) \end{bmatrix}. \tag{4}$$

Then the magnetically induced rotation of the polarization plane reduces to

$$\Delta\rho_{Z'} = \frac{\pi n_b^3}{\lambda} F'_{33} H_{Z'}\,, \tag{5}$$

where $F'_{33} = F_{33}\cos^2\Theta + F_{11}\sin^2\Theta$ denotes the effective Faraday coefficient corresponding to the rotated coordinate system. Then we have

$$F'_{33} = \frac{\lambda}{\pi n_b^3}\left(\frac{\Delta\rho_{Z'}}{H_{Z'}}\right). \tag{6}$$

Finally, the Verdet constant V_F is given by the relation

$$V_F = \frac{1}{\mu_0}\left(\frac{\Delta\rho_{Z'}}{H_{Z'}}\right), \tag{7}$$

where $\mu_0 = 4\pi\times10^{-7}$ N/A^2 is the magnetic constant. Hence, one can determine the Verdet constant V_F and the effective

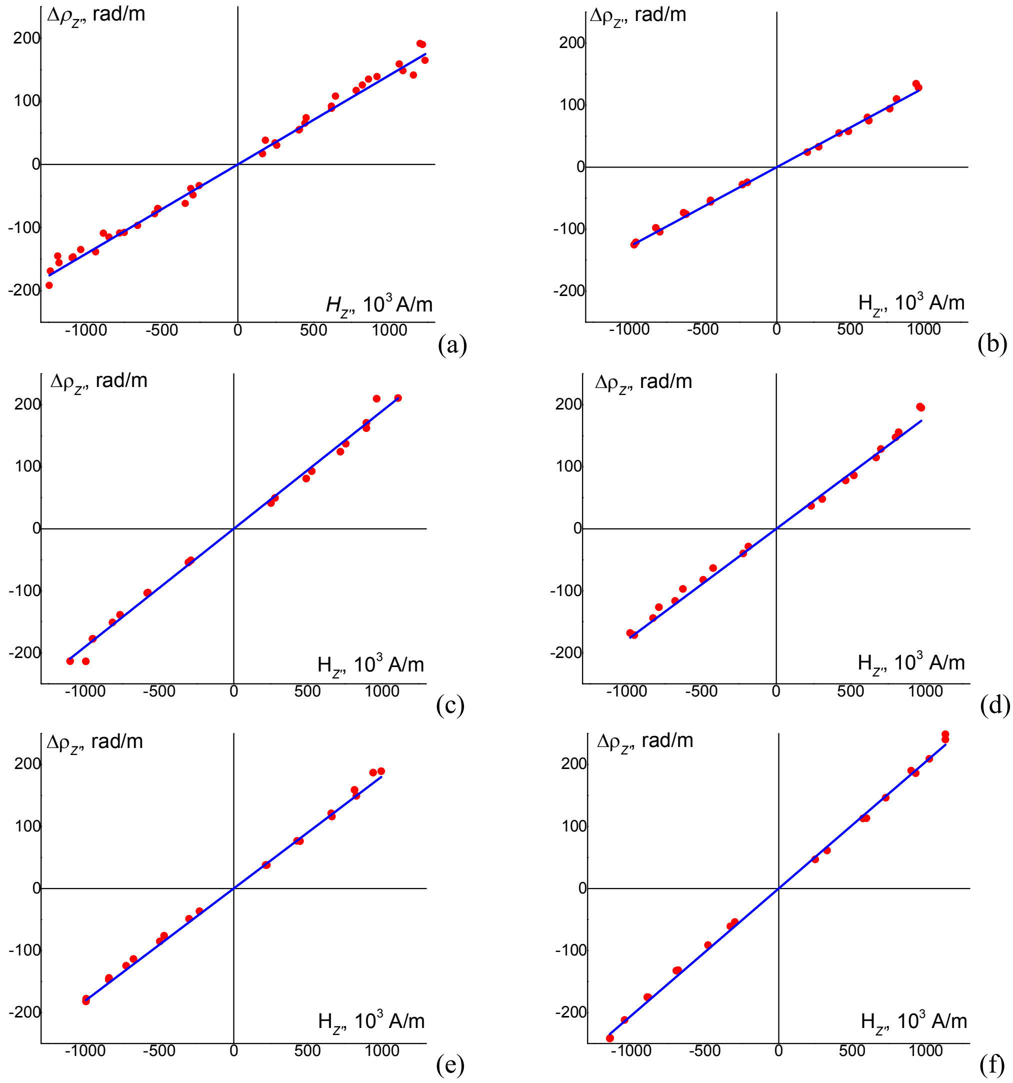


Fig. 1. Dependences of specific optical rotatory power on the magnetic field applied to $TlIn(S_{1-x}Se_x)_2$ mixed crystals (λ = 632.8 nm): (a) x = 0 [19], (b) x = 0.02, (c) x = 0.06, (d) x = 0.10, (e) x = 0.15, and (f) x = 0.25. Circles correspond to experimental data and solid lines to linear fitting.

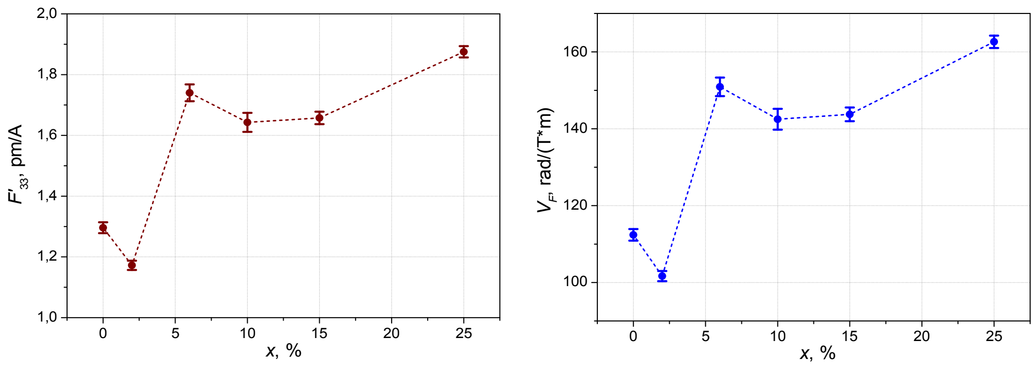
Table 1. Experimental magneto-optical results obtained for the $TlIn(S_{1-x}Se_x)_2$ solid solutions at $\lambda = 632.8$ nm: $(\Delta\rho/H)$ is the slope of dependence of the specific optical rotatory power on the magnetic field, V_F the Verdet constant, F'_{33} the effective Faraday coefficient, Θ the angle between the optic axis and the *c* axis, and *d* the sample thickness.

x	$(\Delta\rho/H)$, mrad/A	V_F, rad/(T×m)	F'_{33}, pm/A	Θ, deg	d, mm
0 (Ref. [19])	141.25±1.88	112.4±1.5	1.296± 0.018	1.3	1.92
0.02	127.76±1.67	101.7±1.3	1.172±0.015	1.7	0.91
0.06	189.64±3.03	150.9±2.4	1.740±0.028	1.4	1.35
0.10	179.04±3.41	142.5±2.7	1.643±0.031	1.3	3.55
0.15	180.64±2.24	143.7±1.8	1.658±0.021	1.5	1.42
0.25	204.36±2.02	162.6±1.6	1.875±0.019	0.9	1.71

Faraday coefficient F'_{33}, using a simple direct experimental measurement of optical rotatory power for the light propagating along one of the optic axes. Note that the main measurement procedures have been described in Ref. [19] for a particular case of pure $TlInS_2$ crystals.

The experimental dependences of specific optical rotation at the wavelength $\lambda = 632.8$ nm upon the external magnetic field applied to the $TlIn(S_{1-x}Se_x)_2$ mixed crystals are presented in Fig. 1. These dependences have been fitted using a standard linear regression procedure, resulting in the effective Faraday coefficients F'_{33} and the appropriate Verdet constants V_F. Table 1 displays these magneto-optical parameters, along with the sample thicknesses and the tilt angles Θ of the optic axis.

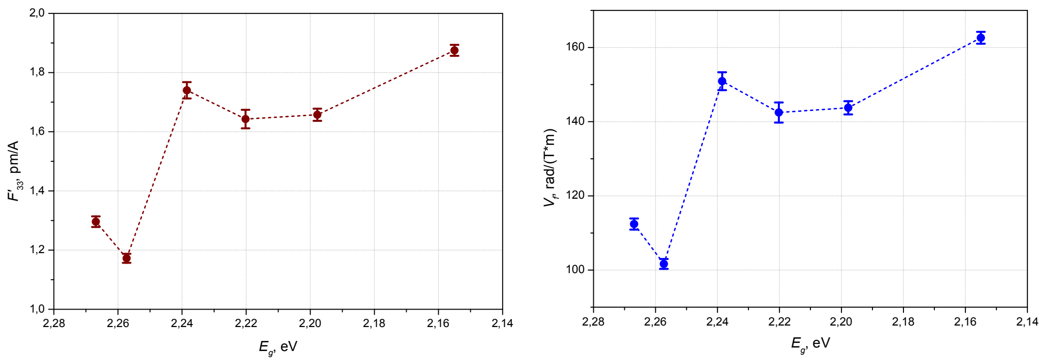
Dependences of the effective Faraday coefficients F'_{33} and the Verdet constants V_F on the Se concentration x are presented in Fig. 2. It is known from the compositional dependences of bandgap E_g determined in Ref. [20] for the $TlIn(S_{1-x}Se_x)_2$ crystals that E_g decreases from 2.27 eV to 2.16 eV when the content of selenium atoms increases from $x = 0$ to 0.25. This means that the absorption edge shifts from $\lambda_{edge} = 548$ nm (green region) at $x = 0$ to $\lambda_{edge} = 575$ nm (green-yellow region) at $x = 0.25$, i.e. it approaches the light wavelength used in our experiments ($\lambda = 632.8$ nm). Therefore the increase in the effective Faraday coefficient and the Verdet constant occurring with increasing Se concentration, which is seen in Fig. 2, could be explained by impending absorption edge and normal dispersion of the coefficients mentioned above. As follows from the conoscopic observations [18], the solid solutions with $x = 0.02$ are somewhat inhomogeneous. This can lead to higher errors of the Faraday coefficient and the Verdet constant found for this particular compound, which can hardly be taken into account (see Fig. 2).



a) b)

Fig. 2. Dependences of effective Faraday coefficient F'_{33} (a) and Verdet constant V_F (b) on Se concentration x for the $TlIn(S_{1-x}Se_x)_2$ solid solutions ($\lambda = 632.8$ nm).

Basing on the data presented in Ref. [19], we have recalculated the dependences depicted in Fig. 2 into the dependences of magneto-optic parameters on the bandgap E_g (see Fig. 3). It is quite expected that both the effective Faraday coefficient and the Verdet constant increase with decreasing bandgap.



a) b)

Fig. 3. Dependences of effective Faraday coefficient F'_{33} (a) and Verdet constant V_F (b) on the bandgap energy E_g for the $TlIn(S_{1-x}Se_x)_2$ mixed crystals (λ = 632.8 nm).

3. Conclusion

In the present work we have studied experimentally the Faraday effect in the monoclinic $TlIn(S_{1-x}Se_x)_2$ solid solutions with the selenium concentration x ranging from 0 to 0.25. Five compounds with $x = 0$, 0.02, 0.06, 0.10, 0.15 and 0.25 have been used. The Verdet constant V_F and the effective Faraday coefficient F'_{33} have been determined at the light wavelength $\lambda = 632.8$ nm under normal conditions. We have shown that the both parameters tend to increase with increasing Se concentration. This behaviour can be successfully explained by dispersion of the Faraday coefficients and a shift of the absorption edge towards longer wavelengths, which occurs with increasing selenium amount.

Acknowledgement

The authors acknowledge financial support of the present study from the Ministry of Education and Science of Ukraine under the Project #0117U006454.

References

1. Panich A M, 2008. Electronic properties and phase transitions in low-dimensional semiconductors. J. Phys.: Condens. Matter. **20**: 293202.
2. Kashida S and Kobayashi Y, 1999. X-ray study of the incommensurate phase of $TlInS_2$. J. Phys.: Condens. Matter. **11**: 1027–1035.
3. Delgado G E, Mora A J, Perez F V and Gonzalez J, 2007. Crystal structure of the ternary semiconductor compound thallium gallium sulfide, $TlGaS_2$. Physica B. **391**: 385–388.
4. Gasanly N M, Mavrin B N, Sterin K E, Tagirov V I and Khalafov Z D, 1978. Raman study of layer $TlGaS_2$, β–$TlInS_2$, and $TlGaSe_2$ crystals. Phys. Stat. Sol. (b). **86**: K49–K53.
5. Müller D, Eulenberger G and Hahn H, 1973. Über ternäre Thalliumchalkogenide mit Thalliumselenidstruktur. Zeitschrift für anorganische und allgemeine Chemie. **398**: 207–220.
6. Isaacs T J, 1975. Determination of the crystal symmetry of the polymorphs of thallium indium disulfide, $TlInS_2$. Zeitschrift für Kristallographie – Cryst. Mater. **141**: 104–108.
7. Aliev R A, Allakhverdiev K R, Baranov A I, Ivanov N R and Sardarly R M, 1984.

Ferroelectricity and structural phase transitions in the crystals of $TlInS_2$ family. Fiz. Tverd. Tela. **26**: 1271–1276.
8. Vakhrushev S B, Zhdanova V V, Kvyatkovskii B E, Okuneva N M, Allakhverdiev K R, Aliev R A and Sardarly R M, 1984. Incommensurate phase transition in a $TlInS_2$ crystal. JETP Lett. **39**: 291–293.
9. Gololobov Y P, Borovoy N A, Isayenko G L and Polovina A I, 2009. Ferroelectric phases in the polytypes of $TlInS_2$ ternary compound. Phys. Stat. Sol. (c). **6**: 989–992.
10. Alekperov O Z, Ibragimov G B, Nadjafov A I and Fakix A R, 2009. Polytypes in ferroelectric $TlInS_2$ and its dielectric and optic properties. Phys. Stat. Sol. (c). **6**: 977–980.
11. Bakhyshov N A, Gasanly N M, Yavadov B M, Tagirov V I and Efendiev S M, 1979. Mixed one- and two-mode behaviour of optical phonons in $TlGaS_{2x}Se_{2(1-x)}$ and $TlInS_{2x}Se_{2(1-x)}$ layer solid solutions. Phys. Stat. Sol. (b). **91**: K1–K3.
12. Gasanly N M, Dzhavadov B M, Tagirov V I and Vinogradov E A, 1979. Long-wave lattice vibrations of $TlInS_{2x}Se_{2(1-x)}$ and $TlGaS_{2x}Se_{2(1-x)}$ layer solid solutions. Phys. Stat. Sol. (b). **95**: K27–K30.
13. Allakhverdiev K R, Akhmedzade N D, Tagiev M M, Shirinov M M and Häseler S, 1988. Long-wavelength IR-active phonons in the $TlInS_2$–$TlInSe_2$ system. Phys. Stat. Sol. (b). **148**: K93–K96.
14. Seyidov M Y, Suleymanov R A and Salehli F, 2011. Origin of structural instability in $TlInS_{2x}Se_{2(1-x)}$ solid solutions. Phys. Scripta. **84**: 015601.
15. Seyidov M H Y, Suleymanov R A and Salehli F, 2009. Effect of the "negative chemical" pressure on the temperatures of phase transitions in the $TlInS_2$ layered crystal. Phys. Solid State. **51**: 2513.
16. Gomonnai A V, Petryshynets I, Azhniuk Y M, Gomonnai O O, Roman I Y, Turok I I, Solomon A M, Rosul R R and Zahn D R T, 2013. Growth and characterisation of sulphur-rich $TlIn(S_{1-x}Se_x)_2$ single crystals. J. Cryst. Growth. **367**: 35–41.
17. Say A, Martynyuk-Lototska I, Mys O, Adamenko D, Kostyrko M, Gomonnai O and Vlokh R, 2020. Temperature dependences of optical indicatrix and thermal expansion parameters of TlIn $(S_{1-x}Se_x)_2$ solid solutions (x = 0, 0.02 and 0.06). Ukr. J. Phys. Opt. **21**: 57–64.
18. Adamenko D, Say A, Martynyuk-Lototska I, Mys O, Kostyrko M, Gomonnai O O, Gomonnai A V and Vlokh R, 2020. (X, T)-phase diagram of TlIn $(S_{1-x}Se_x)_2$ solid solutions (x = 0, 0.02, 0.06, 0.10, 0.15 and 0.25). Temperature dependences of thermal expansion and optical anisotropy parameters. Phase Trans. **93**: 935-944.
19. Adamenko D, Vasylkiv Y, Pogodin A, Kokhan O and Vlokh R, 2017. Faraday effect in $TlInS_2$ crystals. Ukr. J. Phys. Opt. **18**: 197–200.
20. Gasanly N M, 2010. Effect of temperature and isomorphic atom substitution on optical absorption edge of $TlInS_{2x}Se_{2(1-x)}$ mixed crystals ($0.25 \le x \le 1$). Cryst. Res. Technol. **45**: 525–528.

Adamenko D., Krupych O., Kostyrko M., Vasylkiv Yu., Gomonnai O., Gomonnai A. and Vlokh R. 2020. Faraday effect in $TlIn(S_{1-x}Se_x)_2$ solid solutions (x = 0, 0.02, 0.06, 0.10, 0.15 and 0.25). Ukr.J.Phys.Opt. **21**: 178 – 183. doi: 10.3116/16091833/21/4/178/2020

Анотація. *Експериментально вивчено ефект Фарадея в моноклинних твердих розчинах* $TlIn(S_{1-x}Se_x)_2$ *із концентраціями селену x у межах* $0 \le x \le 0{,}25$. *На довжині хвилі світла* $\lambda = 632{,}8$ *нм за нормальних умов визначено постійну Верде* V_F *і ефективний коефіцієнт Фарадея* F'_{33}. *Показано, що обидва коефіцієнти мають тенденцію до збільшення за умови зростання концентрації Se від 0 до 0,25. Така поведінка пояснюється дисперсією коефіцієнтів Фарадея та зсувом краю поглинання в бік довгохвильового спектрального діапазону, який відбувається зі зростанням вмісту селену.*