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DEPOSITION AND PHYSICAL PROPERTIES OF Cu_6PS_5I-BASED THIN FILMS

Cu_6PS_5I-based thin films were deposited onto silicate glass substrates by non-reactive radio frequency magnetron sputtering. The chemical composition of thin films were determined by energy-dispersive X-ray spectroscopy. Electrical conductivity of Cu_6PS_5I-based thin films was studied depends on chemical composition. Optical transmission spectra of Cu_6PS_5I-based thin films were investigated in the interval of temperatures 77–300 K. Absorption edge spectra and refractive index dispersion were derived from the optical transmission spectra. The variation of the main parameters of Urbach absorption edge and electron-phonon interaction was analysed depends on Cu content in Cu_6PS_5I-based thin films.

Keywords: thin film, magnetron sputtering, electrical conductivity, optical absorption, refractive index

Introduction

Cu_6PS_5I compounds belong to the superionic conductors with argyrodite structure. They are the promising materials for wide application as the solid electrolytes, electrochemical and optical sensors [1-4]. At room temperature they belong to the cubic syngony $F\bar{4}3m$; with temperature decrease two phase transitions occur [5]. Optical properties of Cu_6PS_5I crystals were studied in Refs. [6-8].

It should be noted that the investigation of physical properties of Cu_6PS_5I thin films only begins. For the first time Cu_6PS_5I thin films were obtained and studied in Ref. [9]. Structural investigations show the films to be amorphous and have homogeneous two-dimensional structure. Isoabsorption studies reveal that at T=470 K the Cu_6PS_5I film is partially destructed and detached from the substrate. The influence of annealing on the optical absorption edge parameters of Cu_6PS_5I thin films was investigated in Ref. [10].

In the present paper we report on the deposition of Cu_6PS_5I-based thin films by non-reactive radio frequency magnetron sputtering, investigation of electrical conductivity, optical absorption edge and refractive index dispersion.

Experimental

For sputtering of Cu_6PS_5I-based thin films we used the co-deposition technique from two tilted magnetrons – one equipped with Cu_6PS_5I target (pressed powder) and second with pure Cu target (Fig. 1). The deposition was carried out at room temperature in Ar atmosphere.

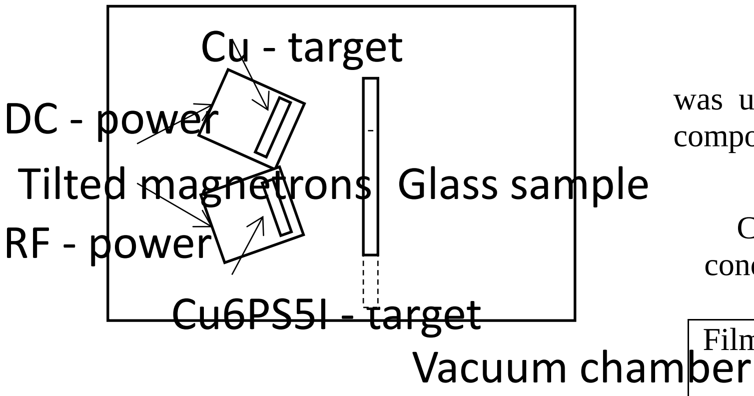

Fig. 1. Schematic drawing of the deposition alignment. Two position of the glass sample are displayed: (1) position during deposition of I and II samples (solid thick line) and (2) position during III samples deposition (dotted thin line).

Structural studies, performed using SEM technique (Hitachi S-4300), confirm the formation of a uniform two-dimensional structure (Fig.2a). At high amount of Cu atoms (Fig.2b) the non-uniformities and structure peculiarities are observed on the film surfaces. Typical AFM-image for $Cu_{5.70}P_{1.61}S_{4.74}I_{0.95}$ thin film is presented in Fig.3.

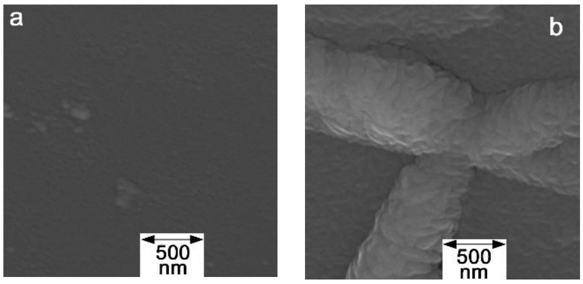

Fig.2. SEM-images for (a) $Cu_{5.46}P_{1.68}S_{5.06}I_{0.80}$ and (b) $Cu_{8.60}P_{0.58}S_{3.14}I_{0.68}$ thin films.

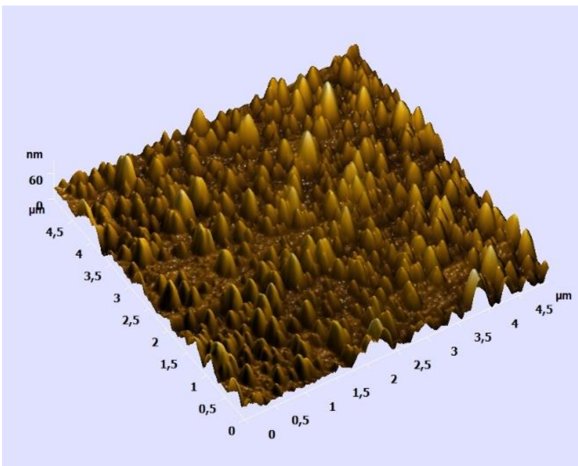

Fig. 3. AFM-image for $Cu_{5.70}P_{1.61}S_{4.74}I_{0.95}$ thin film.

Energy-dispersive X-ray spectroscopy was used to ensure the thin films chemical composition (Table 1).

Table 1

Chemical composition and electrical conductivity for Cu_6PS_5I-based thin films

Films	Chemical composition	Electrical conductivity (σ, S/m)
Sample I		
1	$Cu_{5.37}P_{1.88}S_{5.04}I_{0.71}$	0.044
2	$Cu_{5.46}P_{1.68}S_{5.06}I_{0.80}$	0.047
3	$Cu_{5.56}P_{1.66}S_{4.93}I_{0.85}$	0.049
4	$Cu_{5.70}P_{1.61}S_{4.74}I_{0.95}$	0.051
5	$Cu_{6.77}P_{1.12}S_{3.98}I_{1.14}$	0.056
6	$Cu_{7.55}P_{0.89}S_{3.44}I_{1.12}$	0.066
Sample II		
1	$Cu_{6.31}P_{1.10}S_{4.68}I_{0.91}$	0.053
2	$Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$	0.053
3	$Cu_{6.38}P_{1.11}S_{4.59}I_{0.92}$	0.053
4	$Cu_{6.43}P_{1.15}S_{4.64}I_{0.83}$	0.054
5	$Cu_{6.46}P_{1.1}S_{4.64}I_{0.74}$	0.054
6	$Cu_{6.56}P_{1.11}S_{4.61}I_{0.72}$	0.055
7	$Cu_{6.85}P_{0.99}S_{4.36}I_{0.80}$	0.057
8	$Cu_{7.20}P_{0.83}S_{4.14}I_{0.83}$	0.060
Sample III		
1	$Cu_{7.88}P_{0.73}S_{3.61}I_{0.78}$	0.084
2	$Cu_{8.05}P_{0.68}S_{3.54}I_{0.73}$	0.092
3	$Cu_{8.06}P_{0.69}S_{3.57}I_{0.68}$	0.135
4	$Cu_{8.10}P_{0.65}S_{3.52}I_{0.73}$	0.141
5	$Cu_{8.42}P_{0.60}S_{3.30}I_{0.68}$	0.243
6	$Cu_{8.60}P_{0.58}S_{3.14}I_{0.68}$	0.272
7	$Cu_{8.94}P_{0.56}S_{2.88}I_{0.62}$	0.365
8	$Cu_{9.28}P_{0.50}S_{2.63}I_{0.59}$	0.394

Electrical conductivity was measured by impedancemeter at frequency 1 MHz. Optical transmission spectra of Cu_6PS_5I-based thin films were studied in the interval of temperatures 77–300 K by an MDR-3 grating monochromator, UTREX cryostat was used for low-temperature studies. Spectral dependences of absorption coefficient and dispersion dependences of refractive index of thin films were calculated on their basis.

Results and discussion

Electrical studies have shown that the total electric conductivity of the thin films increase with increase of Cu atoms content. Thus, in with Cu content increase in interval from $Cu_{5.37}P_{1.88}S_{5.04}I_{0.71}$ to $Cu_{9.28}P_{0.50}S_{2.63}I_{0.59}$ the electric conductivity increase from 0.044 S/m to 0.394 S/m, respectively. It should be noted that the total electrical conductivity for the Cu_6PS_5I single crystal is σ_t = 0.13 S/m at 1 kHz [4]. The high value of electrical conductivity in thin films under investigation make them the promising material for creation of solid state batteries and supercapacitors.

Futhermore, with Cu content increase, a red shift of the optical transmission spectra as well as absorption edge spectra is observed (Fig.4). It is shown that the temperature variations of optical transmission in Cu_6PS_5I-based thin films are similar for all investigated samples. With temperature increase, a red shift of both the short-wavelength part of the transmission spectrum (related to the temperature behaviour of the absorption edge) and the interferential maxima is observed. Besides, a typical decrease of transmission in the interferential maxima with temperature is revealed.

Table 2

Parameters of Urbach absorption edge and EPI for Cu_6PS_5I-based thin films

Film	$Cu_{5.46}P_{1.68}S_{5.06}I_{0.80}$	$Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$	$Cu_{8.05}P_{0.68}S_{3.54}I_{0.73}$
E_g^α (300K), eV	2.876	2.521	2.283
E_U (300K), meV	332	256	254
α_0, cm^{-1}	1.32×10^5	1.13×10^6	3.85×10^5
E_0, eV	3.197	3.322	2.802
σ_0	0.131	0.200	0.191
$\hbar\omega_p$, meV	78.2	97.3	91.6
θ_E, K	907	1129	1063
$(E_U)_0$, meV	299	243	239
$(E_U)_1$, meV	652	575	485
$E_g^\alpha(0)$, eV	2.907	2.564	2.313
S_g^α	7.8	18.6	11.1

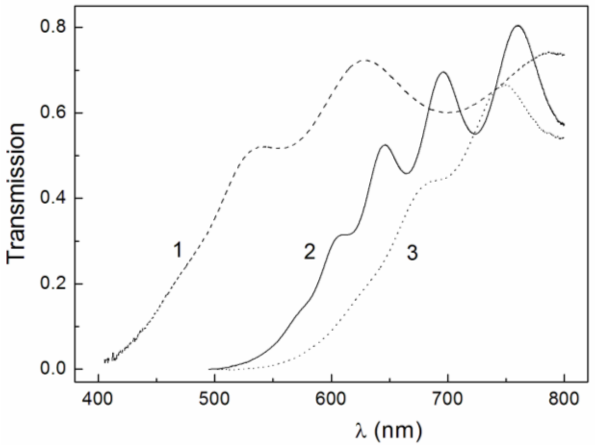

Fig.4. Optical transmission spectra of $Cu_{5.46}P_{1.68}S_{5.06}I_{0.80}$ (1), $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ (2) and $Cu_{8.05}P_{0.68}S_{3.54}I_{0.73}$ (3) thin films at 300 K.

It should be noted that the optical absorption edge spectra of Cu_6PS_5I-based thin films have shown the exponential behaviour (Fig. 5) and their temperature variation described by the Urbach rule [11]

$$\alpha(h\nu,T) = \alpha_o \cdot \exp\left[\frac{\sigma(h\nu - E_0)}{kT}\right], (1)$$

where $E_U = kT/\sigma$ is the Urbach energy, σ is the absorption edge steepness parameter, α_0 and E_0 are the convergence point coordinates of the Urbach bundle. The coordinates of the Urbach bundle convergence point α_0 and E_0 for Cu_6PS_5I-based thin films are given in Table 2.

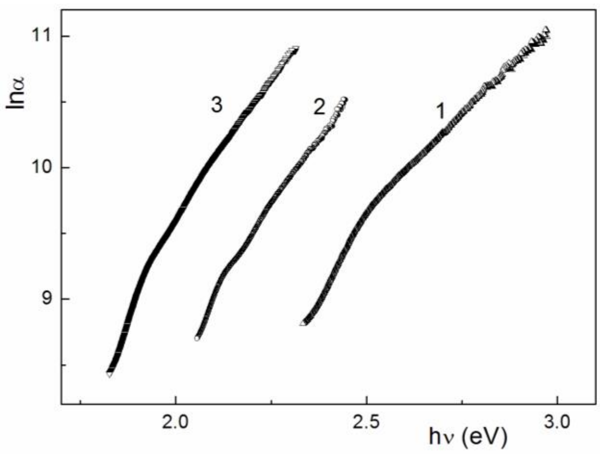

Fig.5. Spectral dependences of the absorption coefficient of $Cu_{5.46}P_{1.68}S_{5.06}I_{0.80}$ (1), $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ (2) and $Cu_{8.05}P_{0.68}S_{3.54}I_{0.73}$ (3) thin films at 300 K.

The temperature behaviour of the Urbach absorption edge in Cu_6PS_5I-based thin films is explained by electron-phonon interaction (EPI) which is strong in the thin films under investigation. The EPI parameters are obtained from the temperature dependence of absorption edge steepness parameter using the Mahr formula [12]

$$\sigma(T) = \sigma_0 \cdot \left(\frac{2kT}{\hbar\omega_p}\right) \cdot th\left(\frac{\hbar\omega_p}{2kT}\right), (2)$$

where $\hbar\omega_p$ is the effective phonon energy in a single-oscillator model, describing the electron-phonon interaction (EPI), and σ_0 is a parameter related to the EPI constant g as $\sigma_0 = (2/3)g^{-1}$ (parameters $\hbar\omega_p$ and σ_0 are given in Table 2). For the Cu_6PS_5I-based thin films $\sigma_0 < 1$ that is the evidence for the strong EPI [13].

It should be noted that in the range of exponential behaviour of optical absorption for their spectral characterisation one can use the energy position of an exponential absorption edge E_g^α at a fixed absorption coefficient α. We used the E_g^α values taken at $\alpha = 5\times10^4$ cm^{-1} for the characterization of the absorption edge spectral position (Table 2). The temperature dependences of E_g^α and the Urbach energy E_U for Cu_6PS_5I-based thin films can be described in Einstein model by relations [14, 15]

$$E_g^\alpha(T) = E_g^\alpha(0) - S_g^\alpha k\theta_E\left[\frac{1}{\exp(\theta_E/T)-1}\right], (3)$$

$$(E_U) = (E_U)_0 + (E_U)_1\left[\frac{1}{\exp(\theta_E/T)-1}\right], (4)$$

where $E_g^\alpha(0)$ and S_g^α are the energy position of absorption edge at 0 K and a dimensionless constant, respectively; θ_E is the Einstein temperature, corresponding to the average frequency of phonon excitations of a system of non-coupled oscillators, $(E_U)_0$ and $(E_U)_1$ are constants. The obtained $E_g^\alpha(0)$, S_g^α, θ_E, $(E_U)_0$, and $(E_U)_1$ parameters for Cu_6PS_5I-based thin films are given in Table 2.

The dispersion dependences of the refractive index for Cu_6PS_5I-based thin films were obtained from the interference transmission spectra (Fig. 6). The slight dispersion of the refractive index is observed in the transparency region while it increases when approaching to the optical absorption edge region.

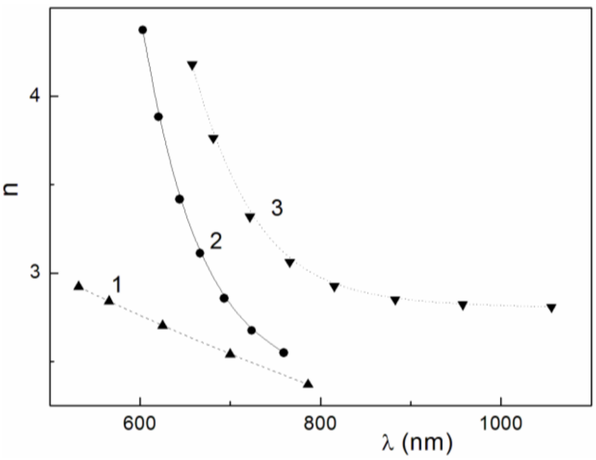

Fig.6. Refractive index dispersions of $Cu_{5.46}P_{1.68}S_{5.06}I_{0.80}$ (1), $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ (2) and $Cu_{8.05}P_{0.68}S_{3.54}I_{0.73}$ (3) thin films at 300 K.

Conclusions

Cu_6PS_5I-based thin films were deposited onto silicate glass substrates by non-reactive radio frequency magnetron sputtering. With Cu content increase, a red shift of the optical transmission spectra as well as increase of the total electric conductivity were observed. The spectral dependences of the absorption coefficient and dispersion dependences of the refractive index were derived from the spectrometric studies of interference transmission spectra. A typical Urbach bundle is observed, the temperature behaviour of the Urbach absorption edge in Cu_6PS_5I-based thin films was explained by strong electron-phonon interaction. With Cu content increase in Cu_6PS_5I-based thin films the decreasing of E_g^α value and Urbach energy E_U, weakening of EPI (increase of σ_0 value) and increasing of effective phonon energy $\hbar\omega_p$, increasing of refractive index and contribution of static structural disorder into E_U were revealed.

REFERENCES

1. Kuhs, W.F., Nitsche, R., Scheunemann K. (1976), "Vapour growth and lattice data of new compounds with icosahedral structure of the type Cu_6PS_5Hal (Hal = Cl, Br, I)", Mater. Res. Bull., Vol. 11, pp. 1115–1124.
2. Nilges, T., Pfitzner, A. (2005), "A structural differentiation of quaternary copper argyrodites: Structure – property relations of high temperature ion conductors", Z. Kristallogr., Vol. 220, pp. 281-294.
3. Studenyak, I.P., Kranjčec, M., Kovacs, Gy.Sh., Desnica, I.D., Panko, V.V., Slivka, V.Yu. (2001), "Influence of compositional disorder on optical absorption processes in $Cu_6P(S_{1-x}Se_x)_5I$ crystals", J. Mat. Res. Vol. 16, pp.1600-1608.
4. Studenyak, I.P., Kranjčec, M., Kurik, M.V. (2006), "Urbach rule and disordering processes in $Cu_6P(S_{1-x}Se_x)_5Br_{1-y}I_y$ superionic conductors", J. Phys. Chem. Solids, Vol. 67, pp. 807-817.
5. Gagor, A., Pietraszko, A., Kaynts, D. (2005), "Diffusion paths formation for Cu ions in superionic Cu_6PS_5I single crystals studied in terms of structural phase transition", J. Solid State Chem, Vol. 178, pp. 3366–3375.
6. Studenyak, I.P., Stefanovich, V.O., Kranjčec, M., Desnica, D.I., Azhnyuk, Yu.M., Kovacs, Gy.Sh., Panko, V.V. (1997), "Raman scattering studies of Cu_6PS_5Hal (Hal = Cl, Br and I) fast-ion conductors", Solid State Ionics, Vol. 95, pp. 221–225.
7. Studenyak, I.P., Kranjčec, M., Kovacs, Gy.Sh., Panko, V.V., Desnica, D.I., Slivka, A.G., Guranich, P.P. (1999), "The effect of temperature and pressure on the optical absorption edge in Cu_6PS_5X (X = Cl, Br, I) crystals", J. Phys. Chem. Solids, Vol. 60, pp. 1897–1904.
8. Kovacs, Gy.Sh., Borets, A.N., Studenyak, I.P., Panko, V.V., Rosola, I.I. (1986), "Optic-refractometric relation and refraction index dispersion in Cu_6PS_5Hal crystals", Ukrainian Journal of Physics, Vol. 31, pp. 1201-1204.

9. Studenyak, I.P., Kranjčec, M., Izai, V.Yu., Chomolyak, A.A., Vorohta, M., Matolin, V., Cserhati, C., Kökényesi, S. (2012), "Structural and temperature-related disordering studies of Cu_6PS_5I amorphous thin films", Thin Solid Films, Vol. 520, pp. 1729-1733.
10. Studenyak, I.P., Kranjčec, M., Chomolyak, A.A., Vorohta, M., Matolin V. (2012), "Optical absorption and refractive properties of superionic conductor Cu_6PS_5I thin films" ["Optychne vbyrannya ta refraktyvni vlastyvosti vidpalenyh tonkyh plivok superionnoho providnyka Cu_6PS_5I"], Nanosystems, nanomaterials, nanotechnologies, Vol. 10, pp. 487-494.
11. Urbach, F. (1953), "The Long-Wavelength Edge of Photographic Sensitivity and of the Electronic Absorption of Solids", Phys. Rev., Vol. 92, pp. 1324-1326.
12. Sumi, H., Sumi, A. (1987), "The Urbach-Martienssen rule revisited", J. Phys. Soc. Japan, Vol. 56, pp. 2211-2220.
13. Kurik, M.V. (1971), "Urbach rule (Review)", Phys. Stat. Sol. (a), Vol. 8, pp. 9-30.
14. Beaudoin, M., DeVries, A.J.G., Johnson, S.R., Laman, H., Tiedje, T. (1997), "Optical absorption edge of semi-insulating GaAs and InP at high temperatures", Appl. Phys. Lett, Vol. 70, pp. 3540-3542.
15. Yang, Z., Homewood, K.P., Finney, M.S., Harry, M.A., Reeson, K.J. (1995), "Optical absorption study of ion beam synthesized polycrystalline semiconducting $FeSi_2$", J. Appl. Phys., Vol. 78, pp. 1958-1963.

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НАПЫЛЕНИЕ И ФИЗИЧЕСКИЕ СВОЙСТВА ТОНКИХ ПЛЕНОК НА ОСНОВЕ Cu_6PS_5I

Тонкие пленки на основе Cu_6PS_5I были нанесены на подложки из силикатного стекла методом нереактивного радиочастотного магнетронного распыления. Химический состав тонких пленок определялся с помощью энергодисперсионной рентгеновской спектроскопии. Электрическая проводимость тонких пленок на основе Cu_6PS_5I изучалась в зависимости от химического состава. Спектры оптического пропускания тонких пленок на основе Cu_6PS_5I исследовались в интервале температур 77–300 К. Спектры края поглощения и дисперсионные зависимости показателей преломления определялись по спектрам оптического пропускания. Изменения основных параметров урбаховского края поглощения и электрон-фононного взаимодействия проанализированы в зависимости от содержания Cu в тонких пленках на основе Cu_6PS_5I.
Ключевые слова: тонкие пленки, магнетронное распыление, электрическая проводимость, оптическое поглощение, показатель преломления

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НАПИЛЕННЯ ТА ФІЗИЧНІ ВЛАСТИВОСТІ ТОНКИХ ПЛІВОК НА ОСНОВІ Cu_6PS_5I

Тонкі плівки на основі Cu_6PS_5I були нанесені на підкладинки з силікатного скла методом нереактивного радіочастотного магнетронного розпилення. Хімічний склад тонких плівок визначався за допомогою енергодисперсійної рентгенівської спектроскопії. Електрична провідність тонких плівок на основі Cu_6PS_5I вивчалася в залежності від хімічного складу. Спектри оптичного пропускання тонких плівок на основі Cu_6PS_5I досліджувалися в інтервалі температур 77–300 К. Спектри краю поглинання та дисперсійні залежності показників заломлення визначалися за спектрами оптичного пропускання. Зміни основних параметрів урбахівського краю поглинання та електрон-фононної взаємодії проаналізовані в залежності від вмісту Cu в тонких плівках на основі Cu_6PS_5I.

Ключові слова: тонкі плівки, магнетронне напилення, електрична провідність, оптичне поглинання, показник заломлення

СПИСОК ВИКОРИСТАНОЇ ЛІТЕРАТУРИ

1. Kuhs W.F., Nitsche R., Scheunemann K. Vapour growth and lattice data of new compounds with icosahedral structure of the type Cu_6PS_5Hal (Hal = Cl, Br, I) // Mater. Res. Bull. – 1976. – Vol. 11. – P. 1115 – 1124.
2. Nilges T., Pfitzner A. , A structural differentiation of quaternary copper argyrodites: Structure – property relations of high temperature ion conductors // Z. Kristallogr. – 2005. – Vol. 220. – P. 281 – 294.
3. Studenyak I.P., Kranjčec M., Kovacs Gy.Sh., Desnica I.D., Panko V.V., Slivka V.Yu., Influence of compositional disorder on optical absorption processes in $Cu_6P(S_{1-x}Se_x)_5I$ crystals // J. Mat. Res. – 2001. – Vol. 16. – P. 1600 – 1608.
4. Studenyak I.P., Kranjčec M., Kurik M.V., Urbach rule and disordering processes in $Cu_6P(S_{1-x}Se_x)_5Br_{1-y}I_y$ superionic conductors // J. Phys. Chem. Solids. – 2006. – Vol. 67. – P. 807 – 817.
5. Gagor A., Pietraszko A., Kaynts D. Diffusion paths formation for Cu ions in superionic Cu_6PS_5I single crystals studied in terms of structural phase transition // J. Solid State Chem. – 2005. – Vol. 178. – P. 3366 – 3375.
6. Studenyak I.P., Stefanovich V.O., Kranjčec M., Desnica D.I., Azhnyuk Yu.M., Kovacs Gy.Sh., Panko V.V. Raman scattering studies of Cu_6PS_5Hal (Hal = Cl, Br and I) fast-ion conductors // Solid State Ionics. – 1997. – Vol. 95. – P. 221 – 225.
7. Studenyak I.P., Kranjčec M., Kovacs Gy.Sh., Panko V.V., Desnica D.I., Slivka A.G., Guranich P.P. The effect of temperature and pressure on the optical absorption edge in Cu_6PS_5X (X = Cl, Br, I) crystals // J. Phys. Chem. Solids. – 1999. – Vol. 60. – P. 1897 – 1904.
8. Kovacs Gy.Sh., Borets A.N., Studenyak I.P., Panko V.V., Rosola I.I., Optic-refractometric relation and refraction index dispersion in Cu_6PS_5Hal crystals // Ukr. Fiz. Zhurnal. – 1986. – Vol. 31. – P. 1201 – 1204.
9. Studenyak I.P., Kranjčec M., Izai V.Yu., Chomolyak A.A., Vorohta M., Matolin V., Cserhati C., Kökényesi S. Structural and temperature-related disordering studies of Cu_6PS_5I amorphous thin films // Thin Solid Films. – 2012. – Vol. 520. – P. 1729 – 1733.
10. Студеняк І.П., Краньчец М., Чомоляк А.А., Ворохта М., Матолін В.. Оптичне вбирання та рефрактивні властивості відпалених тонких плівок суперйонного провідника Cu_6PS_5I // Наносистеми, наноматеріали, нанотехнології. – 2012. – Т. 10. – №3. – С. 489 – 496.
11. Urbach F., The Long-Wavelength Edge of Photographic Sensitivity and of the Electronic Absorption of Solids // Phys. Rev. – 1953. – Vol. 92. – P. 1324 – 1326.

12. Sumi H., Sumi A., The Urbach-Martienssen rule revisited // J. Phys. Soc. Japan. – 1987. – Vol. 56. – P. 2211 – 2220.
13. Kurik M.V., Urbach rule (Review) // Phys. Stat. Sol. (a) . – 1971. – Vol. 8. – P. 9 – 30.
14. Beaudoin M., DeVries A.J.G., Johnson S.R., Laman H., Tiedje T., Optical absorption edge of semi-insulating GaAs and InP at high temperatures // Appl. Phys. Lett. – 1997. – Vol. 70. – P. 3540 – 3542.
15. Yang Z., Homewood K.P., Finney M.S., Harry M.A., Reeson K.J., Optical absorption study of ion beam synthesized polycrystalline semiconducting $FeSi_2$ // J. Appl. Phys. – 1995. – Vol. 78. – P. 1958 – 1963.

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