

Thus, the experimental results obtained, as well as the proposed physical model of the structure of a cluster of nickel atoms, show that not only a new physical phenomenon has been discovered - the diffusion of clusters of impurity atoms in semiconductors, but also the possibility of controlling the state of clusters in semiconductors. This makes it possible to create a new class of photonic materials with bulk superlattices based on semiconductors with ordered clusters, which has unique functional capabilities for creating a new generation of optoelectronic, nanoelectronic, photoelectric devices and sensors of physical quantities. A more comprehensive study of their physical properties can open a number of new physical phenomena that do not exist not only in doped semiconductor materials, but also in semiconductors with clusters of impurity atoms.

REFERENCES

1. Lindroos, Jeanette & Fenning, David P. / Nickel: A very fast diffuser in silicon // Journal of Applied Physics. -2013. - P.7.0021-8979 (printed). DOI: 10.1063/1.4807799.
2. Bakhadyrkhanov M.K. Ismailov K.A. Ismaylov B.K. / Clusters of nickel atoms and controlling their state in silicon lattice // SPQEO. - 2018. - V. 21. N 4. - P. 300–304.
3. Bakhadyrkhanov M.K. Ismaylov B.K. Tachilin S.A. Ismailov K.A. Zikrillaev N.F. / Influence of electrically neutral nickel atoms // SPQEO. - 2020. - V. 23. N 4. - P. 361-365.

OPTICAL ACTIVITY IN Mn DOPED As₂S₃ GLASSES

V. V. Zalamai, A. V. Tiron

*National Center for Materials Study and Testing, Technical University of Moldova, Bv. Stefan cel Mare
168, Chisinau MD-2004, Republic of Moldova
Corresponding author: V.V. Zalamai (victor.zalamai@cnstm.utm.md)*

Spectral dependences of transmittance (T) and wavelength modulated transmittance ($\Delta T/\Delta\lambda$) of As₂S₃ layers doped by manganese (Mn) of different concentrations (0–0.5%) were investigated at temperatures from 10 K to 300 K. Photoluminescence bands at 1.762 eV, 2.107 eV and 2.282 eV due to transition $^4A_{2g}(^4F) \rightarrow ^4E_g(^2G)$, $4T_{1g}(^4G) \rightarrow ^6A_{1g}(^4F)$ and $^4T_{2g} \rightarrow ^6A_{1g}$ of Mn ions, respectively were observed at argon laser excitation. On the luminescence spectra the absorption bands of electron transitions $^6A_{1g}(^4F) \rightarrow ^4T_{1g}(^4G)$ were recognized. The magnitude of refractive index (n) of Mn (0.1 % and 0.5 %) ions doped As₂S₃ layers in low-energy range (1.6–1.9 eV) does not change at temperature decreasing from 300 to 10 K.

Key words: chalcogenide glasses; optical spectroscopy; manganese doping; refractive index; interference spectra.

INTRODUCTION

Chalcogenide glass-like materials attracts an attention of researchers and used as optoelectronics elements in the systems of analytical remote IR spectroscopy and as well as in telecommunications and nonlinear-optics [1]. The glasses activated by transition metal manganese were investigated as phosphors. Manganese ions incorporated in the glass matrix lead to the changes in optical properties and photoluminescence (PL) of material. The self-to-shell emission of manganese ions (especially divalent ion) has a practical interest due to Mn²⁺ ions are the most effective electroluminescent impurity in glasses [1, 2].

For receiving information about impurity ions behavior in a glass structure the corresponding changes of embedded optical characteristics were investigated by methods of Raman and infrared spectroscopies, edge absorption and x-ray spectroscopy [3–6]. In the region of fundamental absorption the incorporated impurities strongly affect the slope and the magnitude of the weak absorption tail. The impurities incorporated in glass matrix depress some lines attributed to matrix defects. This indicates the interaction of activators with the glass matrix. In this case, the maximums near the absorption edge may shift to the short-wavelength region (Dy, Sm) or to the long-wavelength region (Mn) [2, 5].

Manganese ions embedded in a glass matrix are luminescence centers and can have various valences (from +2 to +4). These materials possess well pronounced emitting characteristics from blue to red spectral range (depending on the charge state). In some glasses (borate) the both charge states Mn^{3+} and Mn^{2+} can be simultaneously [7, 8]. In silicate and germanate glasses, the manganese ion have the charge state +2 and situates in octahedral or tetrahedral environment [9]. The Mn^{2+} and Mn^{4+} ions have been identified as activators of luminescence. An investigation of x-ray stimulated oxidation of Mn^{2+} ions in phosphate glasses shows that Mn^{2+} ions plays the role of a sensitizing additive [10]. The Mn^{2+} ions practically do not dye glass in the visible spectral range but the Mn^{3+} ions impart the violet color to the irradiated glass due to the emerging absorption band of the Mn^{3+} ions in the green region of the spectrum [8]. The study of Mn^{2+} ion local environment in various structures is the subject of a significant number of papers [10–17]. This is due to the fact that the Mn^{2+} ions have an intense electron paramagnetic resonance signal and are easily detected in a glass matrix.

In the present work optical properties, edge absorption (transmission), photoluminescence and spectral dependences of refractive indices of glassy As_2S_3 doped with manganese ions were studied. The changing of above-mentioned properties was investigated at temperature range 300–10 K and at different concentration of manganese impurity.

EXPERIMENTAL METHODS

The bulk chalcogenide As_2S_3 glasses were made from initial elements of arsenic and sulfur (5N purity) by traditional melting method with quenching. The adding of transition metal impurity (Mn) into mixture of initial components was used for receiving of doped crystals. The synthesis process taken place in the quartz ampoules vacuumed to 10^{-4} – 10^{-5} Torr and deposited into the horizontal or vertical furnaces with vibrational and rotational mechanisms. Depending on glass composition the synthesis temperatures varied from 700 °C to 1100 °C and the synthesis duration was from 24 to 70 hours. After the synthesis the ampoule with liquid compound was quickly cooled (hardening) in air, in cold water or in liquid nitrogen. The nominal concentration of manganese ions was in the limits 0.01–0.5%. The color of received glasses varied from yellow-red (for undoped As_2S_3) to black (for As_2S_3 glass doped with Mn). Thin films of glasses with different thicknesses were made by vacuum deposition on glass substrates.

Absorption (transmission) and wavelength modulated transmission spectra were measured on MDR-2 spectrometer with linear dispersion 7 Å/mm and aperture 1:2. The low temperature spectra were measured in LTS-22 C 330 optical cryogenic system. Photoluminescence spectra were registered by double large-aperture spectrometer SDL-1 (aperture 1:2 and linear dispersion 7 Å/mm). The input and output slits of monochromators do not exceeded 70 μm i.e. the measurements resolution was ~ 0.5 meV. All optical spectra measurement systems are computerized.

EXPERIMENTAL RESULTS AND DISCUSSION

It is known that intracenter emission from the rare-earth ions levels in materials (glasses), especially divalent manganese, is of practical interest because manganese ions are the most efficient electroluminescent impurity [16]. Especially successful is the use of manganese ions with other rare-earth elements. According Ref. [2] absorption bands of manganese ions are observed at 393, 400 and 413 nm and it can be attributed to next electron transitions $6A_1(^6S) \rightarrow ^4T_2(^4D)$, $6A_1(^6S) \rightarrow ^4E(^4G)$ and $6A_1(^6S) \rightarrow ^4T_2(^4G)$, respective. The absorption of Mn^{2+} ions in the region of 450–465 nm is absent, therefore for luminescent properties; ions of other rare-earth elements are introduced into the system, for example, Eu^{3+} with an absorption band at 465 nm ($^7F_0 \rightarrow ^5D_2$). The excitation of such system by light of wavelength range 450–465 nm is possible due to energy transfer from europium level 5D_2 to manganese level $^4T_2(^4G)$. This indicates that there is an exchange of electrons between the levels of different rare-earth ions.

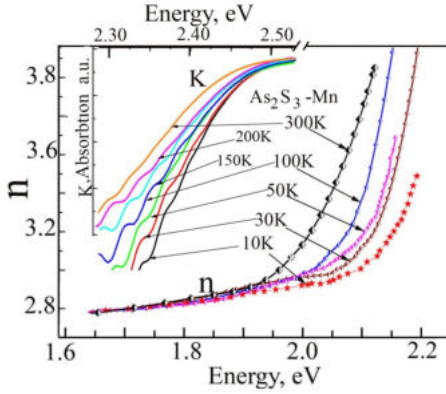


Fig. 1. Spectral dependences of absorption coefficient (K) and of refractive index (n) of As_2S_3 glass doped with Mn of 0.5% concentration measured at different temperatures

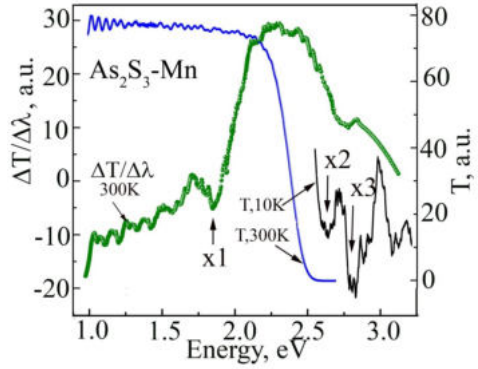


Fig. 2. Spectral dependences of transmission coefficient (T) and of wavelength modulated transmission ($\Delta T/\Delta\lambda$) of As_2S_3 glasses doped with manganese of 0.5% concentration measured at temperatures 300 K and 10 K

With temperature decreasing the edge absorption spectra are changes as one can see in the insert of Figure 1. These spectra were measured for thin layers of As_2S_3 doped by 0.5 % Mn. At low energies in these spectra the slope of the absorption curves changes with temperature. The slope of the curves becomes minimal at temperature 10 K. At energies $E < 2.3$ eV the absorption curve is shifted toward higher energies when temperature decreasing. The same behavior takes place and for the spectral dependences of refractive index. In the energy range $E > 2.3$ eV the absorption graphs tend to energy of 2.5 eV, Fig. 1. Absorption magnitude in this region is formed by the electron transitions between manganese ions levels.

A weak feature x1 at energy 1.776 eV is observed in wavelength modulated transmission spectra in long-wavelength range (see Fig. 2). We believe that electrons transitions from levels $^4A_{2g}(^4F) \rightarrow ^4E_g(^2G)$ of Mn^{4+} ions (1.764–1.778 eV [20]) are appeared in this region. At energies $E > 2.5$ eV some features x2 (2.61 eV), x3 (2.76 eV) and x4 (3.15 eV),

x5 (3.31 eV) and x6 (3.5 eV), fig. 3 were observed in the wavelength modulated transmission spectra.

The maximum x2 observed at energy 2.61 eV is more probably attributed to the absorption by electron transitions from levels ${}^6A_1(S) \rightarrow {}^4T_1(G)$ of Mn^{2+} ions (2.395 eV, [12]). Transitions ${}^4A_2g({}^4F) \rightarrow {}^4T_{2g}({}^4F)$ of Mn^{4+} ions (2.413 eV [20]) are also observed in the same spectral range. The maximum x3 (2.76 eV) is believed to be due to electronic transitions from the ${}^6A_1(S) \rightarrow {}^4T_2(G)$ Mn^{2+} ions levels (2.799 eV, [13]) or ${}^4A_2g({}^4F) \rightarrow {}^2T_{2g}({}^2G)$ transitions of Mn^{4+} ions (2.761 eV [20]).

According data of Ref. [11] the most intensive absorption band of manganese with maximum around 405 nm (3.06 eV) is a superposition of bands of the next energy transitions ${}^6A_1({}^6S) \rightarrow {}^4T_2({}^4D)$, ${}^6A_1({}^6S) \rightarrow E({}^4G)$ and ${}^6A_1({}^6S) \rightarrow {}^4T_2({}^4G)$. Observed absorption band x4 (3.15 eV, fig. 3) is more probably associated with transitions ${}^6A_1({}^6S) \rightarrow {}^4AE_2({}^4D)$ of Mn^{2+} ions (3.141 eV [16]). The maximum x5 at energy 3.31 eV is due to the transitions ${}^4A_2g({}^4F) \rightarrow {}^4T_{1g}({}^4F)$ Mn^{4+} ions (3.308 eV) and x6 by transitions ${}^4A_2g({}^4F) \rightarrow {}^4T_{1g}({}^4F)$ (3.498 eV) [20].

CONCLUSIONS

When photons with an energy range of 2.65–2.89 eV (argon laser lines) are absorbed, an excitation mechanism is realized, the transition of electrons from ${}^4A_{1g}({}^4F)$ to ${}^4T_{2g}({}^4G)$ levels (Mn^{2+} ions) or from ${}^4A_{2g}({}^4F)$ to ${}^4T_{2g}({}^4G)$ (Mn^{4+} ions). Charge carriers migrate nonradiatively between ion levels. The recombination of electrons from ${}^4T_{2g}({}^4G)$ to ${}^4A_{2g}({}^4F)$ or to ${}^6A_{1g}({}^4F)$ levels appears as a luminescence band at 2.282 eV. At energies of 2.127 eV, a weaker luminescence band associated with transitions ${}^4T_{1g}({}^4G) \rightarrow {}^6A_{1g}({}^4F)$ is observed. At energies of 2.192 eV, a narrow dip (absorption band) is detected on the contour of a wide band of luminescence spectra. This feature is associated with an absorption of emitted energy (photoluminescence) by electron transitions between levels ${}^6A_{1g}({}^4F) \rightarrow {}^4T_{1g}({}^4G)$.

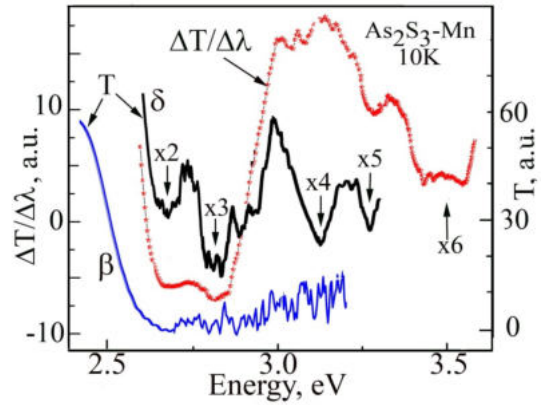


Fig. 3. Transmission (T) and of wavelength modulated transmission ($\Delta T/\Delta\lambda$) spectra of As_2S_3 layers ($d = 1.5 \mu m$, curve β) and nanolayers ($d = 350 nm$, curve δ) doped with Mn of 0.5 % concentration measured at 10 K

REFERENCES

1. E.M. Dianov, M.Yu. Petrov, V.G. Plotnichenko, V.K. Sysoev, Estimation of the minimum possible optical loss in chalcogenide glasses. *Quantum Electron.* 9(4). (1982) 798.
2. V.F. Aguekian, Intracenter transitions of iron group ions in semiconductor matrices of II - VI type. *Physics of the Solid State* 44(11) (2002) 1921–1939.
3. K. Tanaka, T. Gotoh, N. Yoshida, S. Nonomura, Photothermal deflection spectroscopy of chalcogenide glasses, *Journal of Applied Physics* 91(1) (2002) 125–128.
4. G.C. Righini, M. Ferrari, Photoluminescence of rare-earth-doped glasses, *La Rivista del Nuovo Cimento* 28(12) (2005) 53.
5. Simas Šakirzanovas, Novel $\text{Sm}^{2+/3+}$ Phosphors as Luminescence Converters for Near UV Radiation, Doctoral Thesis, Physical Sciences, Chemistry (03 P), Vilnius (2011) 112.
6. J.M.P. Almeida, C. Lu, C.R. Mendonca and C.B. Arnold, Single-step synthesis of silver sulfide nanocrystals in arsenic trisulfide, *Optical Materials Express*, 5(8) (2015) 241289.
7. S. Lee, M.-T. Trinh, J.-R. Nam, K.-S. Lim, M. Lee, E. Kim, Laser-induced defect centers and valence state change of Mn ions in sodium borate glasses, *J. Lumin.* 122-123 (2007) 142–145.
8. G.V. Rao, P.Y. Reddy, N. Veeraiah, Thermoluminescence studies on $\text{Li}_2\text{O}-\text{CaF}_2-\text{B}_2\text{O}_3$ glasses doped with manganese ions, *Mater. Lett.* 57 (2002) 403–408.
9. A. Van Die, A.C.H.I. Leenaers, W.F.V.J. Der Weg, Germanate glasses as hosts for luminescence of Mn^{2+} and Cr^{3+} , *Non-Cryst. Solids.* 99 (1988) 32–44.
10. A. Murali, R.P.S. Chakradhar, J.L. Rao Allowed and forbidden hyperfine structure of Mn^{2+} ions in sodium tetraborate glasses – an EPR and optical study, *Physica B.* 358 (2005) 19–26.
11. V. Singh, R.P.S. Chakradhar, J.L. Rao, D.-K. Kima, EPR and luminescence properties of combustion synthesized $\text{LiAl}_5\text{O}_8:\text{Mn}$ phosphors, *Mater. Chem. Phys.* 110 (2008) 43–51.
12. R.W.A. Franco, J.F. Lim, C.J. Magon, J.P. Donoso, Y. Messadde, Magnetic resonance study of the crystallization behavior of InF_3 -based glasses doped with Cu^{2+} , Mn^{2+} and Gd^{3+} , *J. Non-Cryst. Solids.* 352 (2006) 3414–3422.
13. P.E. Menassa, D.J. Simkin, Spectroscopic investigations of Mn^{2+} in sodium borosilicate glasses, *J. Lumin.* 35 (1986) 223–233.
14. I. Bratu, I. Ardelean, A. Barbu, V. Mih, D. Maniu, G. Botezan, Spectroscopic investigation of some lead phosphate oxide glasses containing manganese ions, *J. Molec. Struct.* 482–483 (1999) 689–692.
15. R.V.S.S.N. Ravikumar, K. Ikeda, A.V. Chandrasekhar, Y.P. Reddy, P.S. Rao, J. Yamauchi Ravikumar, Site symmetry of Mn(II) and Co(II) in zinc phosphate glass, *J. Phys. Chem. Solids.* 64 (2003) 2433–2436.
16. D.L. Griscom, R.E. Griscom, Paramagnetic Resonance of Mn^{2+} in Glasses and Compounds of the Lithium Borate System, *J. Chem. Phys.* 47 (1967) 2711–2722.
17. C. Sumalatha, B. Sreedhar, M. Yamazaki, T. Takeuchi, K. Mori, K. Kojima, ESR and optical absorption studies of Mn^{2+} ions doped silica and germania gels, *J. Non-Cryst. Solids.* 203 (1996) 84–87.
18. N.F. Mott and E.A. Davis, *Electronic Processes in Non-crystalline Materials* Clarendon Press: Oxford Univ. Press, Oxford, 1971; 437 pp.
19. H. Sobotta, V. Riede, Bestimmung der optischen Konstanten aus Reflexions- und Durchlassigkeitsmessungen im fernen Infrarot am Beispiel des $n\text{-GaAs}$, *Wiss. Z. Karl-Marx-Univ. Leipzig, Math.-Naturwiss. R.*, 20 (1971) 147. [in German].
20. M. Srivastava, Mikhail G. Brik, Samuel J. Camardello, Holly A. Comanzo, and Florencio Garcia-Santamaria, Optical Spectroscopy and Crystal Field Studies of the Mn^{4+} Ion (3d3) in the Double Perovskite NaLaMgTeO_6 *Z. Naturforsch.* 2014, 69b, 141–149.