M. F. Bulaniy, A. V. Kovalenko, A. S. Morozov, E. G. Plakhtiy, O. V. Khmelenko

Oles Honchar Dnipro National University, Dnipro, Ukraine
**e-mail: kovalenko.dnu@gmail.com*

LIFETIME OF ELECTRONS IN EXCITED STATES OF ION Mn^{2+} IN ZnS:Mn CRYSTALS

The spectral dependence of current photoconductivity in ZnS:Mn crystals and temperature dependences of photoconductivity measured in maximums of the excitation spectrum of photoconductivity (λ_{excit}= 395, 430, 470, 490, and 530 nm) are researched. The positions of five excited levels and ground-state level of Mn^{2+} ion in ZnS band-gap are determined. The lifetime of electrons in the excited states of Mn^{2+} ion depending on the concentration of activator is investigated. The longest lifetime of electrons in the excited states τ of ~1.72 – 1.75 ms was observed in ZnS crystals with the activator concentration C_{Mn}~ 5×10^{-4} – 10^{-3} g/g.

Keywords: lifetime of electrons, ZnS:Mn crystals, excited states of ion Mn^{2+},spectral dependence of current photoconductivity, temperature dependences of current photoconductivity.

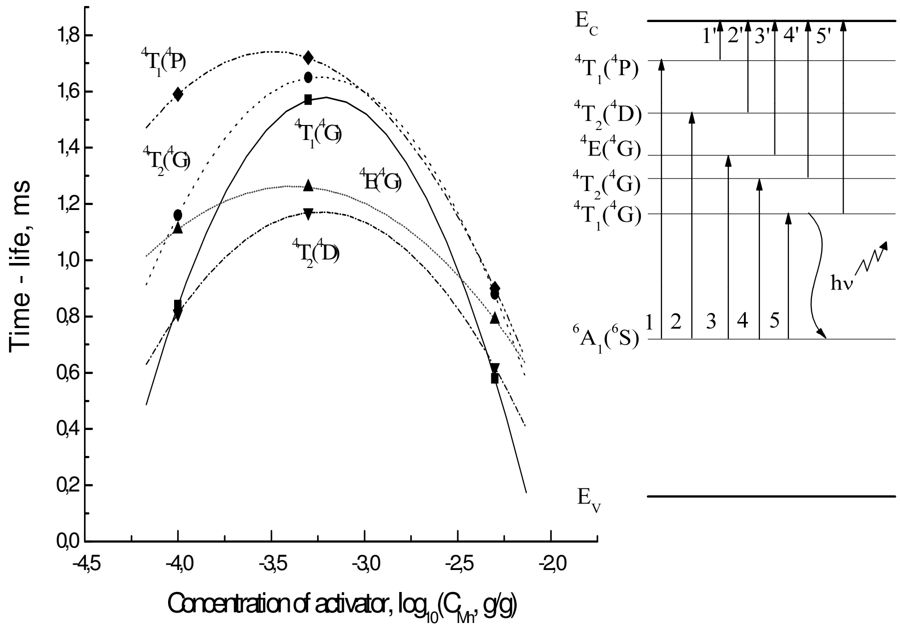
1. Introduction

Zinc sulphide doped by ions Mn^{2+} attracts attention of researches for a long time to its broad possibilities of practical application as effective luminescent material in orange spectral region [1, 2]. Also, as well known, ZnS crystals doped with ions of Cu are a good luminescent material in the green emission band [3], Al – in the blue one [4]. Nowadays the interest in zinc sulphide gained an additional impulse in connection with the use of nanocrystals of connections of A_2B_6 type for development of white light sources, improvement of properties of modern radiate structures. Being introduced in the active layers of semiconductor light-emitting diodes, lasers, quantum amplifiers, nanocrystals as quantum dots, they substantially increase the quantum exit of luminescence, correct the form of radiation spectra [5].

The further improvement of properties of optoelectronic devices of the new generation requires the detailed information about energy of electronic levels responsible for radiation transitions and data about the excited states of radiation centers and lifetime of electrons in these states.

2. Experimental results and discussion

In ZnS crystals Mn^{2+} ions create five energy levels related to the excited states [2, 6]. The radiative transition with a maximum in the spectral region 580 – 595 nm (Fig.1) is connected with the electron relaxation from the lower excited state ($^4T_1$) to the ground state ($^6A_1$). It is necessary to emphasize that the wavelength of a radiative transition depends on the concentration of Mn^{2+} ions and also on the local environment of a radiation center in the crystal lattice of ZnS crystals. In its turn it determines the fact that the radiation spectrum of Mn^{2+} ion in zinc sulphide is nontrivial one and it is possible to distinguish at least five elementary bands of photoluminescence with λ_{max}= 557, 578, 600, 616, and 637 nm, accordingly [2].



(a) (b)

Fig. 1. Dependence of lifetime of electrons in the excited states of Mn^{2+} ions on the concentration of activator in samples (a), energy diagram of electronic levels of Mn^{2+} ion in the forbidden band of ZnS:Mn crystals (b).

It is possible to estimate the energy position of the excited states of Mn^{2+} ion relative to the ground state (transitions 1 – 5 in Fig.1) by analyzing the spectra of absorption and spectra of excitation of photoluminescence in ZnS:Mn crystals. These spectra coincide practically [2] and wavelengths that correspond to the transitions 1 – 5 in Fig. 1 correspond to λ_{excit}= 395, 430, 470, 490, and 530 nm. Let us determine energy gaps between the bottom of the conduction band of ZnS crystals (E_c level) and excited states of Mn^{2+} ion (transitions 1' – 5' in Fig. 1). These data are obtained on the basis of analyzing the spectral dependence of current photoconductivity (I_{ph}) of ZnS:Mn crystals (Fig. 2) and temperature dependences of photoconductivity in the crystals measured in maximums of the spectral band of photoconductivity excitation (Fig. 3). There are two maximums in the spectral dependence of excited current of photoconductivity in selfactivated ZnS crystals, which are connected with absorption edge and electron excitation in the conduction band from shallow acceptor levels. Additional five maximums in spectral dependence the excitations current of photoconductivity connected with the excited states of Mn^{2+} ion, reliably register in ZnS:Mn crystals with the large concentration of manganese: C_{Mn}~ 5×10^{-2}g/g (Fig. 2). The position of these maximums coincides with that of maximums in the absorption spectrum and in the excitation spectrum of photoluminescence of ZnS:Mn crystals.

On the basis of the temperature dependences of current photoconductivity, measured in these maximums (Fig. 3), we determined the activation energies of electrons in the conduction band from the levels of the excited states of Mn^{2+} ion. The results of these measurements are tabulated in Table 1. On the one hand, the obtained data allow to set the position of the whole complex of energy levels of Mn^{2+}ion relative to the E_c level.

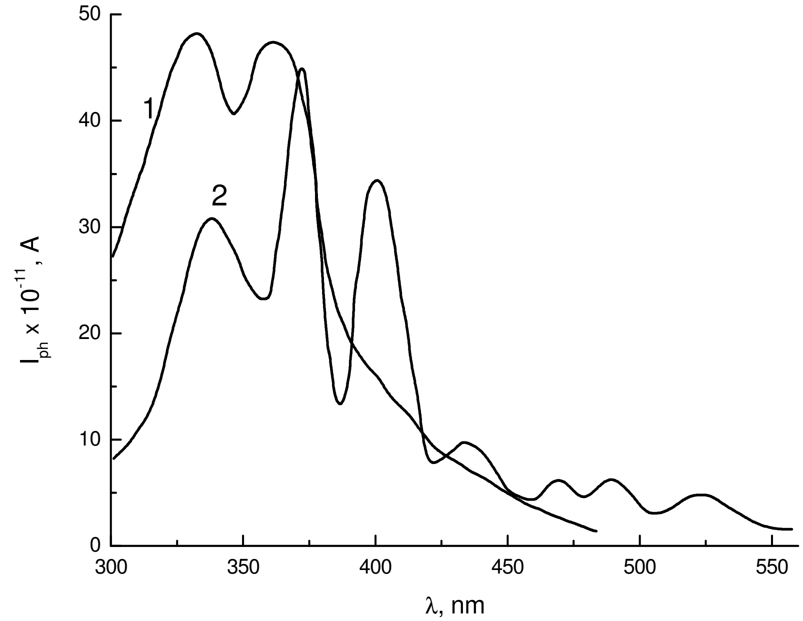


Fig. 2. Spectral dependence of current photoconductivity at T = 300K : 1 –selfactivated ZnS crystal, 2 – ZnS:Mn crystal with the concentration of activator $C_{Mn}= 5\times10^{-2}$ g/g

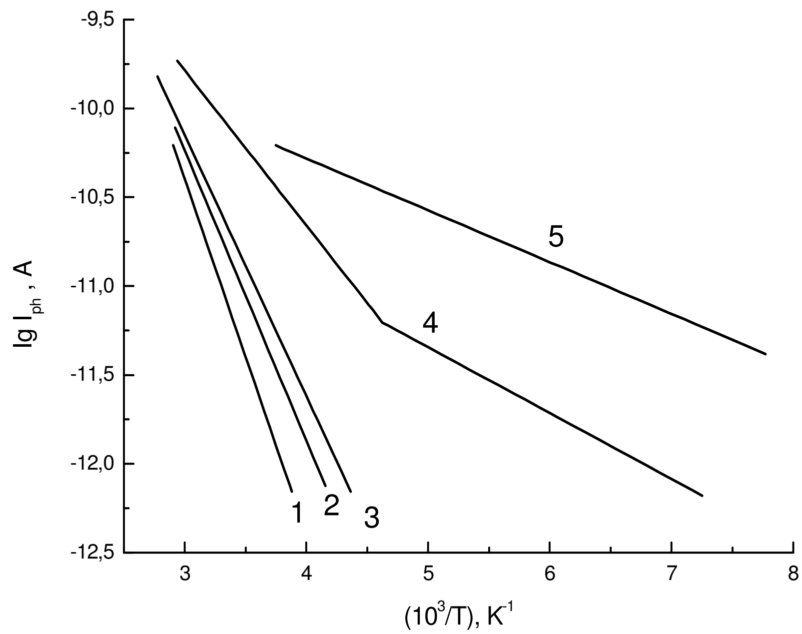


Fig. 3.Temperature dependence of current photoconductivity in ZnS:Mn crystals with the concentration of activator $C_{Mn}= 5\times10^{-2}$ g/g : 1 – λ_{excit}= 530 nm, 2-λ_{excit}= 490 nm, 3 - λ_{excit}= 470 nm, 4 - λ_{excit}= 430 nm and 5 - λ_{excit}= 395 nm.

Table 1.

Energies of activation of the excited levels of Mn^{2+} ion in zinc sulphide

Wavelength in a maximum of excitation of photoconductivity, nm	Energy of quanta of excitant light, eV (transitions 1-5 in fig.1)	Activation energy, eV (transitions 1^{I}-5^{I} in fig.1)	Denotation of the excited states of Mn^{2+} ion ZnS
395 ± 5	3.14 ± 0.04	0.12 ± 0.02	$^4T_1$ (^4P)
430 ± 5	2.88 ± 0.02	0.37 ± 0.02	$^4T_2(^4D)$
470 ± 5	2.64 ± 0.03	0.57 ± 0.02	$^4E(^4G)$
490 ± 5	2.52 ± 0.02	0.68 ± 0.02	$^4T_2(^4G)$
530 ± 5	2.34 ± 0.02	0.85 ± 0.02	$^4T_1(^4G)$

On the other hand, the research allows to estimate an energy gap between the ceiling of valence band of ZnS (E_v level) crystals and ground - state of Mn^{2+} ion level $^6A_1$ (^6S). Taking on a value of band - gap of zinc sulphide equals 3,7 eV, transitions energy 5 and 5' in fig.1 2,34 and 0,85 eV, accordingly (see Table 1), we obtain, that the ground- state position of Mn^{2+} ion is 0.51 eV higher than the valence band ceiling of ZnS crystals.

Conclusions

Experimental results show that processes of photoluminescence decreasing in ZnS:Mn crystals after influence of impulse of exciting radiation are well described by established dependences. This fact and also obtained information about the position of the complex of energy levels of Mn^{2+} ion in the band-gap of zinc sulphide allows to determine not only the lifetime of electrons in the excited states of Mn^{2+} ions, but also the dependence of this parameter on the activator concentration (Fig. 1). During our experiments the excitation of photoluminescence was conducted by impulses of light with the duration τ ~ 40 mcs and energy of quanta corresponding to the energy transitions 1 – 5 in Fig. 1. The longest lifetime of electrons in the excited states τ~1.72 – 1.75 ms was observed in ZnS crystals with the activator concentration C_{Mn}~5×10^{-4} – 10^{-3} g/g.

References

1. **Korsunskaya, N. E.** Osobennosti legirovaniya poroshkoobraznogo ZnS primes'yu Mn v processe sinteza i posleduyushchego otzhiga/ N. E. Korsunskaya, Yu. Yu. Bacherikov, T. P. Stara, V. P. Klad'ko, N. P. Baran, Yu. O. Polishchuk, A. V. Kuchuk, A.G. Zhuk, E.F. Venger // PHTP . – 2013. – Vol. 47, No. 5. – P. 702 – 709.
2. **Bulaniy, M. F.** Margantsevi tsentri viprominyuvannya v monokristallakh sul'fidu zinku/ M. F. Bulaniy, O. V. Kovalenko, S. O. Omelchenko, A. R. Omel'chyuk, O. S. Morozov // Fizika i khimiya tverdogo tila . – 2011. – Vol. 12, No. 3. – P. 573 – 578.
3. **Bol, A. A.** Luminescence of nanocrystalline ZnS: Cu 2+ / A.A. Bol, J.Ferwerda, J.A. Bergwerff, A. Meijerink //Journal of Luminescence. – 2002. – Vol. 99, No. 4. – P. 325 – 334.
4. **Prathap, P.** Preparation and characterization of transparent conducting ZnS: Al films/ P. Prathap, N. Revathi, Y. V. Subbaiah , K. R. Reddy, R. W. Miles //Solid State Sciences. – 2009. . – Vol. 11, No. 1. – P. 224 – 232.
5. **Korbutyak, D. V.** Svitloviprominyuyuchi vlastivosti kvantovikh tochok napivprovidnikovikh spoluk A_2B_6 / D.V. Korbutyak, O.V. Kovalenko, S.I. Budzulyak, S.M. Kalitchuk, I.M. Kunchak //UFG. – 2012. – Vol. 7, No. 1. – P. 42 – 95.
6. **Prokof'ev, T. A.** Mekhanizmi vozbugdeniya photoluminescencii ionov Mn^{2+} v kristallakh ZnS:Mn./ T. A. Prokof'ev, B. A. Polezhaev, A. V. Kovalenko // ZHPS. – 2005. – Vol. 72, No. 6. – P. 788 – 793.

Received 15.11.2017