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Role of Auger-Type Energy Transfer Processes in Quenching of Anti-Stokes Emission in Chromium and Iron Doped ZnSe: ODMR, Optical and Time-Resolved Study

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Energy up-conversion in chromium and iron doped ZnSe results in the appearance of an anti-Stokes luminescence. The process is efficient in ZnSe:Cr, but not in ZnSe:Fe. We conclude that very efficient three-center Auger processes in ZnSe:Fe quench the anti-Stokes luminescence emission. For chromium doped samples influence of the Auger mechanism is weaker, which we explain by less efficient carrier retrapping by Cr ions. We further discuss possibility of efficient pumping of infrared Cr-related emissions via Cr photoionization transition.

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1. Introduction

Difficulties in achieving efficient stimulated emission at short wavelengths motivated an intensive research in this field. At present GaN-based structures are

used for blue-violet laser diodes. Earlier, up-conversion materials were considered as a possible alternative solution. In these materials blue or violet emission is obtained under optical pumping with light sources of a lower energy, preferably with a red color GaAs-based laser diodes, if we want to construct compact light emitting devices. The so-obtained up-converted emission is often referred to as an anti-Stokes luminescence (ASL). Energy up-conversion should be efficient at room temperature. Moreover, the so-obtained short wavelength emission should have power of not less than a few mW, to be of any practical use. The latter means that efficiency of light conversion should be of at least few times 10^{-3}, considering that for practical applications ASL should be pumped with a laser diode.

We achieved the required efficiency for chromium doped ZnSe [1]. However, the ASL in ZnSe:Cr is efficient only at low temperatures and we obtained the required efficiency only when pumping with a green line (514.25 nm) of an argon laser. The latter is due to an unfavorable location of the Cr^+ charge state in ZnSe band gap. The ASL was excited by two-step ionization transitions via Cr^+ charge state of chromium. First photon (of the energy above 2.0 eV) populates this state, generating free holes in the valence band. The second photon (of the same energy) photoionizes Cr^+ state, inducing free electrons in the conduction band, i.e., both free electrons and free holes are photogenerated, which, if trapped by shallow centers, can participate in the anti-Stokes emission.

Practically any impurity, which introduces a band gap state, should be active in the ASL processes. In this work we discuss properties of ASL emission in iron doped ZnSe. This impurity introduces a mid gap level in ZnSe. Photoionization energy is optimized for a two-photon optical pumping with a red color GaAs-based laser diodes.

Considering that Cr and Fe show similar photoionization rates, we expected similar efficiencies of the ASL processes in ZnSe. Unfortunately, we found that the ASL process in ZnSe:Fe is very inefficient, which we explain by a very efficient Auger-type energy transfer from the ASL active centers to iroń centers.

2. Results and discussion

In Fig. 1 we compare the ASL spectra observed in chromium and iron doped ZnSe. The spectra were recorded under optimal conditions for the anti-Stokes excitation. In ZnSe:Cr the ASL is due to shallow donor–shallow acceptor pair (DAP) transitions [1]. Origin of the ASL in ZnSe:Fe is not clear. This emission is too weak to get any conclusive identification. From its spectral position we assume that this emission is of identical origin as the ASL in ZnSe:Cr.

Whereas in ZnSe:Cr the ASL is relatively bright, the one which we observe for ZnSe:Fe is surprisingly weak. Its efficiency is by far too low to be of any practical interest. Estimated by us quantum efficiency of the energy up-conversion in ZnSe:Fe is about 10^{-5}, i.e., it is by two orders in magnitude too low for any

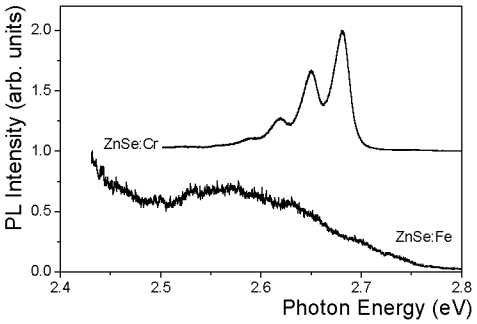

Fig. 1. Band edge part of the photoluminescence in ZnSe:Cr and ZnSe:Fe measured at liquid helium temperature under the anti-Stokes excitation.

practical applications. This was a very puzzling observation, since we expected that efficiency of the ASL in Cr or Fe doped ZnSe is similar, since the optical cross-sections for ionization transitions of Cr and Fe are quite similar. We performed several experiments to explain this puzzling observation.

First we measured excitation dependence of the ASL efficiency. Whereas in ZnSe:Cr the ASL shows a linear dependence on excitation intensity, it shows a quadratic dependence in the case of an undoped ZnSe and also ZnSe:Fe, as is shown in Fig. 2. A linear dependence of the ASL intensity can be observed if a photopopulated band gap level is metastable [1]. In fact, the photoexcited Cr^+ charge state is metastable at low temperatures, as we observed in the electron spin resonance (ESR) investigations. Only for the ZnSe samples annealed in zinc vapors Cr^+ recombination with free holes is too efficient to observe the metastable Cr^+ ESR signal. Annealing in zinc reduces concentration of acceptors centers due to zinc vacancies, i.e., reduces concentration of trap levels of free holes, which increases rate of retrapping of free holes by Cr^+ centers.

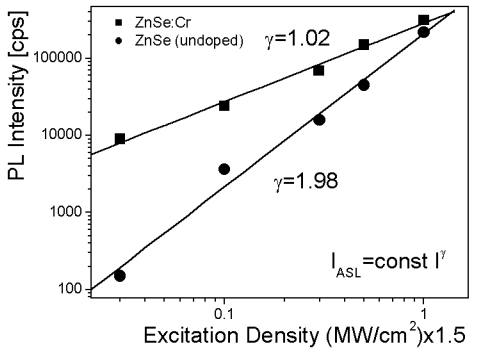

Fig. 2. Excitation power dependence of the shallow donor–shallow acceptor pair emission in undoped ZnSe, and in Cr doped samples. In the latter case the DAP emission was excited at the ASL conditions.

Our photo-ESR investigations indicate that the photoexcited Fe^{3+} charge state decays fast even at liquid helium temperature. This we observed earlier for ZnS:Fe and explained by a high efficiency of the so-called bypassing process [2, 3]. By bypassing process we mean here efficient retrapping of free electrons and holes by Fe centers. We propose that this process also explains why the ASL is weak in ZnSe:Fe. If photogenerated free carriers are retrapped by Fe centers, they are not trapped by shallow donor and acceptor centers, which are active in the ASL.

If even a small part of free carriers is trapped at shallow donor and acceptor centers in ZnSe:Fe, the ASL should be observed and should show a similar PL decay time, as the one in Cr-doped samples, or as a shallow DAP emission in an undoped ZnSe. This is not the case, as we show in Fig. 3, in which we compare the PL/ASL decay spectra observed for undoped ZnSe (PL), and for the ASL in ZnSe:Cr and ZnSe:Fe. The latter two decay spectra were measured under the conditions optimized for the anti-Stokes excitation. The shortest decay is observed for ZnSe:Fe. Thus, the ASL in ZnSe:Fe is not only very weak, but also shows a very different PL kinetics.

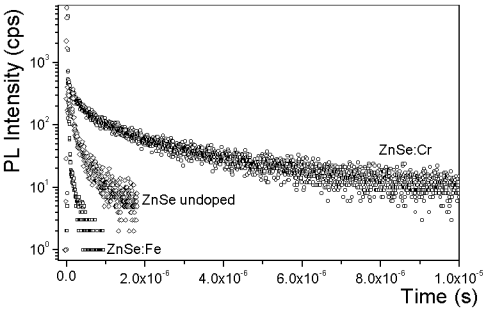

Fig. 3. PL kinetics of the ASL emission in ZnSe:Cr and ZnSe:Fe, as compared to the PL decay of shallow DAP emission in undoped ZnSe observed under the above band gap excitation.

The difference indicates that in ZnSe:Fe the ASL is quenched by some very efficient process of a nonradiative recombination. Possible explanation comes from the photo-ESR study. We observed that Fe^{3+} charge state is photoinduced under illumination, which ionizes deep ZnSe acceptors, i.e., in the process generating free electrons. Part of electrons is trapped by shallow donors active in DAP emission, rest by Fe^{3+} centers. Thus, such illumination should rather quench Fe^{3+} ESR signal. Surprisingly Fe^{3+} ESR signal is photoexcited. We observed similar conditions of the Fe^{3+} excitation in ZnS:Fe and explained by the Auger-type energy transfer from photoexcited DAPs to Fe centers [2]. The process is of Auger-type, since Fe is ionized due to the transfer from DAPs. The process is referred to as three centers (donor, acceptor, and Fe) Auger process [2–4].

Based on the present study we claim that the difference between the ASL kinetics in Cr and Fe doped ZnSe relates to differences in efficiency of three centers Auger processes. Formally Auger-type energy transfer should be equally efficient in these two cases, since the efficiency of the transfer is proportional to a spectral overlap of DAP emission and Fe or Cr ionization. This spectral overlap is fairly similar for Fe and Cr doped ZnSe.

To explain the difference, we first checked if the Auger process is active in ZnSe:Cr. That was not simple, since for Cr doped samples ESR experiments are not conclusive. Photoexcitation, which ionizes deep acceptors and generates free electrons in the conduction band, can excite Cr^{+} due to trapping of electrons by Cr^{2+} or by Auger-type transfer, which ionizes Cr^{2+}. In both cases Cr^{+} is detected in the photo-ESR study.

To clear this point we proposed the following optically detected magnetic resonance (ODMR) experiment. In the ODMR experiment we set detection at one of the two Cr^{2+} intrashell infrared emissions (with maxima at 0.95 μm and 2.47 μm) and studied at which magnetic resonance conditions these emissions are enhanced. The idea of the experiment was simple. If Auger processes are efficient, any process, which enhances DAP recombination, should also increase rate of Cr ionization. Part of photoexcited Cr^{+} centers retraps free holes, which as we found from PL experiments, induces intrashell transitions of chromium 2+.

Results of the ODMR study are shown in Fig. 4. Three magnetic resonance signals are detected. The most pronounced one, with g-factor of about 1.1, is due to magnetic resonance at shallow donors in ZnSe. We relate two other signals to magnetic resonances of acceptor centers. All signals are observed as an increase in the intensity of the Cr^{2+} infrared emissions.

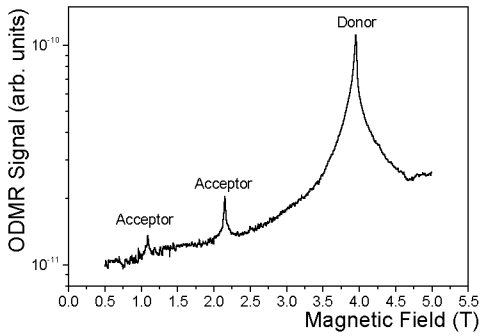

Fig. 4. 60 GHz ODMR spectrum detected via an increase in the intensity of the Cr-related near-infrared PL emission.

As explained, detection of donor and acceptor resonance signals via Cr intrashell emissions indicates that energy transfer from DAP to Cr must be efficient. The mechanism explaining the present ODMR results is the following: by flipping a spin of either donor or acceptor we enhance DAP recombination. DAPs can de-

cay either radiatively or nonradiatively, the latter most likely via an Auger-type energy transfer to Cr ions, as suggested by a magnitude of a spectral overlap between DAP emission and Cr ionization transitions.

ODMR thus confirms that the Auger process is also active in ZnSe:Cr. Comparison of spectral overlaps suggests similar efficiency of the process in ZnSe:Fe and ZnSe:Cr. Contrary, the PL investigations indicate that the process cannot be efficient in ZnSe:Cr, since the ASL in ZnSe:Cr is fairly bright.

This contradiction can be explained assuming that free holes, which are created in the valence band under the 2+ to 1+ chromium ionization, are efficiently retrapped by acceptors active in the ASL, as is shown in Fig. 5. Then, the Auger-type energy transfer will only recycle carriers (trapping — DAP decay — Cr ionization/neutralization — carrier retrapping, and so on) and thus will only delay the ASL decay, as is in fact observed in the PL kinetics. Only if free carriers are retrapped by transition metal (TM) ions, the DAP emission is quenched. Simple model calculations indicate that quenching of the PL intensity should then be observed together with a shortening of the PL decay time τ. The latter effect is described by

$$\tau^{-1} = \beta_{\mathrm{DAP}} + \gamma_{\mathrm{TCAR}} N_{\mathrm{TM}},$$

where β_{DAP} is DAP recombination rate, γ_{TCAR} is the Auger process rate and N_{TM} is concentration of TM impurity.

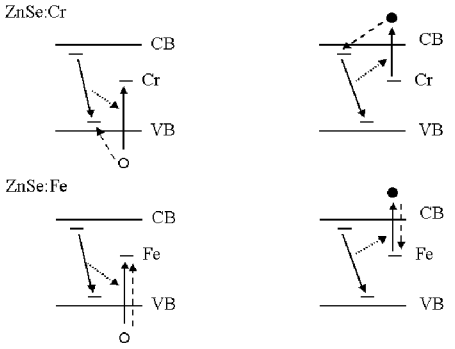

Fig. 5. Model of the Auger type energy transfer processes in ZnSe:Cr and ZnSe:Fe. The influence of the process on the shallow DAP emission depends on a rate of retrapping of photoionized free carriers by shallow centers active in the DAP transitions.

At increased temperatures shallow donor and acceptor centers active in the ASL are no longer efficient trap centers. Carriers can be thermally ionized from these centers back to the bands, before radiative or nonradiative recombination can occur. Then the rate of their recombination via TM ions increases. In the consequence, DAP-to-TM energy transfer can now more efficiently quench the ASL.

Important consequence of the latter is that recombination of free carriers via Cr^{2+} intrashell transitions becomes enhanced at increased temperatures. Then the Cr^{2+} intrashell emissions are efficiently pumped under the Cr photoionization. This observation can have important consequences for optimization of a tunable laser emission of ZnSe:Cr under optical pumping [5–9].

3. Conclusions

Fe and Cr show very different carrier trapping rates in ZnSe. In the consequence, Cr doped samples can be used as a nonlinear material showing efficient energy up-conversion, whereas in Fe doped samples the ASL is weak. Differences in trapping rates result in very different efficiency of the Auger-type nonradiative processes in ZnSe:Cr and ZnSe:Fe.

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