



Photoluminescence dynamics of Co-doped $Zn_{1-x}Cd_xSe$ and ZnS_xSe_{1-x} crystals

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Abstract

Intra-shell d–d relaxation processes of Co^{2+} -centres are investigated by means of time-integrated and time-resolved photoluminescence spectroscopy. The composition dependence of the luminescence and the decay of the Co L-line in ZnCdSe and ZnSSe alloys is presented for the first time. Additionally, new Co-related infrared luminescence lines were observed near 1.6 eV. Taking into account the energy position of the L-line and the relaxation dynamics of the green and the infrared luminescence, the L-line is explained as an internal doublet–quartet d–d transition of the Co-centres. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Transition-metals (TMs) act as a killer of the visible luminescence. TMs can also be used to achieve high resistivity. Most of these ions, like cobalt and nickel, present a multiplet structure in both II–VI and III–V compounds [1]. Some of

their spectroscopic features are well explained by ligand field theory [2]. However, the microscopic model of a Co-related luminescence at 2.36 eV in ZnSe – the L-line – is a subject of controversy [2,3].

Investigations of Co in ternary compounds are very attractive because changes of the physical properties with varying composition can be studied systematically. Also, there exists only a little information about TMs in ternary alloys. The most interesting effects expected in the alloys are variations of conduction and valence band edges and

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the modified overlap of the d-orbitals of the transition metal with the p-orbitals of the anions of the host crystal. A variation of the L-line oscillator strength should occur.

To study these effects we investigated the luminescence and the relaxation dynamics of the ternary alloys ZnCdSe:Co and ZnSSe:Co with varying Zn/Cd and S/Se composition.

2. Experimental procedure

The $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ and $\text{ZnS}_x\text{Se}_{1-x}$ samples were grown by the chemical transport method in a wide composition range of Cd ($x = 0.0\text{--}0.5$) and S ($x = 0.0\text{--}1.0$). The Co concentration of all samples except the ZnS-sample is $1 \times 10^{18} \text{ cm}^{-3}$. The Co-content of the ZnS-sample is $3 \times 10^{20} \text{ cm}^{-3}$.

As excitation source for photoluminescence and time-resolved measurements, we used a pulsed dye-laser operating at 442 nm with a repetition frequency of 3.8 MHz, a quasi-cw output power of 50 mW and less than 3 ps pulse duration. The luminescence was detected at 2 K with a subtractive spectrometer and a micro-channel plate.

The time-resolved measurements were performed using the single-photon-counting technique. The recorded transients were corrected by subtracting the background and fitted using up to three exponential decays.

Micro-Raman measurements were carried out in order to verify the systematic change of the ternary alloy composition and the homogeneity of the crystals.

3. Results

The luminescence spectra of the alloys with relatively small Cd or S content are dominated by the L-line which was known previously only for binary ZnSe:Co [1–3]. In Fig. 1 the L-line with its phonon replica is presented for alloys with a Cd-content varying up to 5% and a S-content up to 30%. In both cases the energy position of the L-line decreases with increasing content of Cd or S, respectively. A broadening of the L-line is also observed.

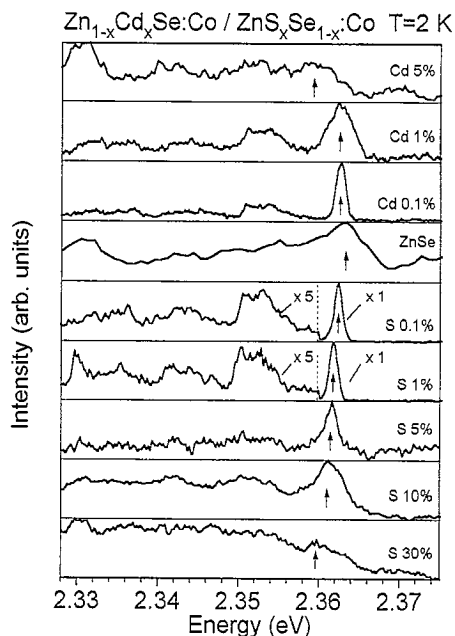


Fig. 1. Photoluminescence of ZnSe:Co, ZnCdSe:Co and ZnSSe:Co mixed crystals in the region of the L-line under excitation with a dye laser at 442 nm. The L-line position is marked by an arrow in each spectrum. An increasing content of Cd or S causes a shift of the L-line to lower energies and a broadening of the zero-phonon line.

The decay time of the L-line and the corresponding transients of the ternary compounds $\text{ZnS}_x\text{Se}_{1-x}$ are shown in Fig. 2. It can be seen that an increasing S-content (verified by Raman measurements) leads to a continuously faster relaxation of the emission.

As an example, Fig. 3a shows the infrared luminescence recorded near 1.6 eV on $\text{ZnS}_{0.001}\text{Se}_{0.999}$. The indicated decay times were derived from the transients shown in Fig. 3b. Comparing the relaxation of the L-line and the infrared luminescence of $\text{ZnS}_{0.001}\text{Se}_{0.999}$:Co, the emission lines at 1.6 eV can be divided into two groups because of their dynamic behaviour. The first group (1.673, 1.656 and 1.578 eV) has – within the experimental error of 30 ps – the same decay time as the L-line (320–350 ps). For the second group of lines (1.632 and 1.622 eV) the decay time of about 20 ps

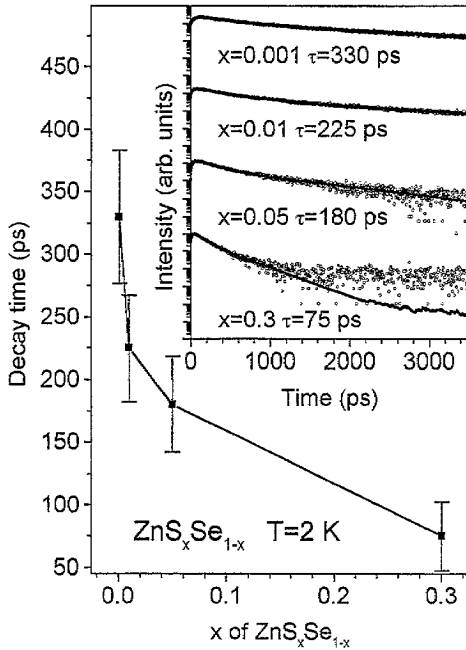


Fig. 2. Photoluminescence kinetics of the L-line in $\text{ZnS}_x\text{Se}_{1-x} : \text{Co}$ mixed crystals under excitation with a dye laser at 442 nm. The increasing S content leads to a continuously decreasing decay time of the luminescence indicated for each sample (error bars: < 30 ps).

was observed, that is one order of magnitude smaller than that of the L-line.

The decay of the L-line and of the infrared luminescence lines was fitted using a single exponential decay. For the approximated relaxation dynamics an error less than 10 ps plus 5% of the fitted value has to be considered. The multi-exponential parts of the transients are caused by the incompletely removed background.

4. Discussion

The measured decay times, composed of radiative and nonradiative components, can be described by the formula:

$$\frac{1}{\tau_{\text{measured}}} = \frac{1}{\tau_{\text{radiative}}} + \frac{1}{\tau_{\text{nonradiative}}}$$

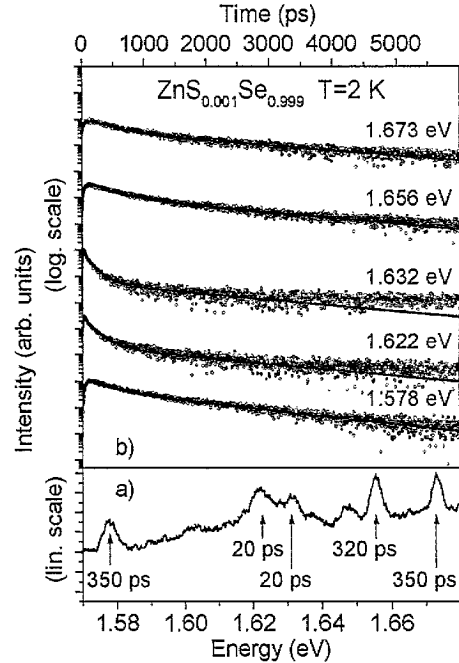


Fig. 3. (a) Infrared emission of the $\text{ZnS}_{0.001}\text{Se}_{0.999} : \text{Co}$ sample under excitation with a dye laser at 442 nm. Several luminescence lines are marked and the decay times are indicated. (b) The transients of the 1.6 eV luminescence lines of $\text{ZnS}_{0.001}\text{Se}_{0.999} : \text{Co}$ under excitation with a dye laser at 442 nm are shown. Due to their decay time these lines are attributed to transitions from excited doublet and quartet states to different quartet-ground-states, respectively.

We assume that the nonradiative processes in the Co multiplet system are (analogous to Ni, Cu and Fe in ZnS and CdS [4]) dominated by multiphonon processes. The efficiency of the nonradiative processes depends strongly on the number of phonons involved in the multiphonon process. Referring to Fig. 1, the changes of the energy positions of the L-line in the alloys are small compared to the phonon energies ($E_{\text{TO}} = 25\text{--}26\text{ meV}$, $E_{\text{LO}} = 31\text{--}30\text{ meV}$), i. e., the energy difference for the multiphonon processes is nearly independent of the composition. Furthermore, the decay times of the L-line decrease for Cd- and S-contents varying from $x = 0.01$ up to 0.05 while the TO and LO phonon energies (taken from Raman measurements) either decrease or remain

constant within an accuracy of 0.05 meV. Thus, with nearly constant energy difference and phonon energies, we expect the nonradiative decay time caused by the multiphonon processes to be equal to first order for these samples. The rapid change of decay times observed should therefore be attributed to a change of the radiative recombination processes.

In the model which assigns the L-line to an intra-shell ${}^2\Gamma\text{-}{}^4\text{A}_2(\text{F})$ transition of Co [2,3] the decreasing decay time with increasing Cd- or S-content can be explained as follows: In the ZnCdSe-alloys an increasing Cd-content causes a decreasing band gap leading to a hybridisation of the excited ${}^2\Gamma$ -state involved in L-line luminescence with the s-states of the conduction band accompanied by a faster relaxation of the luminescence. As for ZnSSe alloys, the decreasing lattice constant with increasing S-content causes a stronger interaction of the Co-centre with the ligand atoms. Thus, an increase of the oscillator strengths of intra-shell transitions caused by an increasing overlap of the d-orbitals of the Co-centre with the p-orbitals of the neighbouring S-atoms is expected.

It is important to understand how the new infrared luminescence lines near 1.6 eV (Fig. 3) fit into this model. In this energy range, the ${}^4\text{A}_2(\text{F})\text{-}{}^4\text{T}_1(\text{P})$ transition is well known from absorption measurements [2]. We used time-resolved measurements to determine whether the all infrared lines described above have the same nature. One group of lines near 1.6 eV shows the same decay time as the L-line. In our interpretation the L-line is related to an intra-shell Co^{2+} -transition from an unidentified ${}^2\Gamma$ doublet state to the ground ${}^4\text{A}_2(\text{F})$ quartet state. It should be noticed that the energy difference between the ${}^4\text{T}_1(\text{F})$ and the ${}^4\text{A}_2(\text{F})$ state is 0.7 eV [2]. Consequently, the transition from the ${}^2\Gamma$ doublet state involved in the L-line to the ${}^4\text{T}_1(\text{F})$ state should occur at 1.6 eV and should have the same decay time of luminescence as the L-line. In view of the much faster decay of the other group of infrared luminescence lines, we assign the latter lines to allowed transitions to the ground state of Co^{2+} . Keeping in mind the quartet symmetry of the ground state and the absorption measurements, we propose the transition ${}^4\text{T}_1(\text{P})\text{-}{}^4\text{A}_2(\text{F})$.

We should mention that the interpretation of the L-line as a Co-bound deep exciton [3] would face severe problems. First, it is expected that the lifetime of bound excitons grows with the increase of binding energy [5]. In the case of ZnSSe:Co the lifetime decreases with the increasing exciton binding energy due to the increasing band gap. Furthermore, it would be difficult to explain why the decay time of Co-related transitions in the infrared region should be the same as that of a bound exciton.

In summary, we interpret the L-line and the infrared lines having the same decay time as intra-shell doublet-quartet transitions in the Co^{2+} -

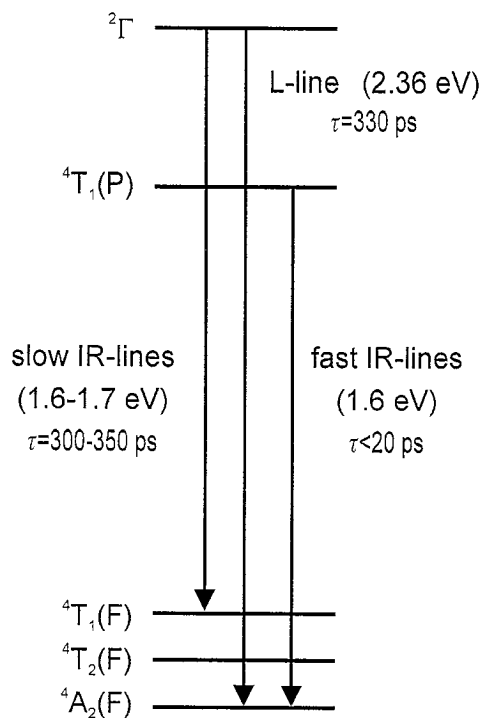


Fig. 4. Proposed energy-level scheme of the Co-related radiative transitions in ZnCdSe and ZnSSe alloys. The L-line and the related group of infrared lines have equal decay times because they involve the same excited doublet state ${}^2\Gamma$. The doublet-quartet transition is allowed by the admixture of p-orbitals of the ligand atoms and forbidden by spin. Referring to their faster relaxation, the second group of infrared lines is assigned to a ${}^4\text{T}_1(\text{P})\text{-}{}^4\text{A}_2(\text{F})$ quartet-quartet transition. The decay times measured for $\text{ZnS}_{0.001}\text{Se}_{0.999}:\text{Co}$ are given.

centre (Fig. 4). The fast infrared luminescence is assigned to a quartet–quartet transition of Co^{2+} in the ternary II–VI compounds.

Acknowledgements

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