VUV spectroscopy of wide band-gap crystals doped with rare earth ions

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Abstract

Spectral and kinetic properties of vacuum ultraviolet (VUV) luminescence from different fluoride crystals doped with Nd^{3+}, Er^{3+} or Tm^{3+} are discussed. Concentration quenching of VUV luminescence, the impact mechanism of the energy transfer from the matrix to the emission centers as well as nonradiative relaxation processes in the rare earth ions have been detected and studied. The crystal properties are analyzed from the viewpoint of their possible applications as materials for fast VUV scintillators and VUV solid state lasers. Only some of Nd^{3+} doped crystals possess simultaneously both high light output and relatively good timing properties of VUV luminescence and such crystals can be considered as promising materials for fast VUV scintillators. On the other hand, many of Er^{3+} and Tm^{3+} doped fluoride crystals are very attractive candidates as active media for tunable VUV solid state lasers with optical pumping. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The development of new efficient solid-state emitters in the vacuum ultraviolet (VUV) spectral range is an important and promising field of research for both scintillation and laser techniques. To move towards the development of new VUV scintillators and VUV solid state lasers, it is necessary first of all to characterize spectroscopic properties of various combinations of wide band-gap hosts and doping ions displaying optical activity in the VUV spectral range. In this context, wide band-gap fluoride crystals doped with some trivalent rare earth (RE) ions with parity-allowed interconfiguration 5d–4f radiative transitions, for example Nd^{3+}, Er^{3+} and Tm^{3+}, can offer the exceptional possibility for designing new VUV emitting materials [1].

In the present paper appropriate spectroscopic properties of some wide band-gap crystals doped with Nd^{3+}, Er^{3+} or Tm^{3+} have been studied and

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analyzed from the viewpoint of their possible applications as materials for fast VUV scintillators and as active media for VUV solid state lasers.

2. Experiment

The studies of emission and excitation spectra as well as luminescence decay kinetics were performed at the SUPERLUMI station of HASY-LAB under the excitation by the 5–30 eV synchrotron radiation from the DORIS storage ring at DESY (Hamburg) [2]. The VUV luminescence was detected with a 0.5 m Pouey-type secondary VUV monochromator (with an instrumental resolution of about 1 nm) equipped with a solar-blind photomultiplier for spectral measurements and a microsphere plate detector for measurements of decay curves. The time correlated single-photon counting was used for the measurements of time-resolved spectra and luminescence decay curves with a time resolution of 0.3 ns.

Single crystals of different fluorides doped with Nd^{3+}, Er^{3+} or Tm^{3+} were grown by using the vertical Bridgman [3] and hydrothermal synthesis techniques [4].

3. Results and discussion

The VUV luminescence of Nd^{3+}, Er^{3+} or Tm^{3+} ions doped into wide band-gap crystals is due to interconfiguration transitions from the lowest level of the $4f^{n-1}5d$ configuration to different levels near the ground state of the $4f^{n}$ configuration [5]. The luminescence spectrum of a $LiKYF_5$ crystal doped with Nd^{3+} is shown in Fig. 1. The broadband luminescence in the spectrum corresponds to interconfiguration $4f^2 5d$–$4f^3$ transitions while the narrow lines observed at $\lambda > 200$ nm are due to intraconfiguration $4f^3$–$4f^3$ transitions in the Nd^{3+} ion (the assignments of emission bands to particular transitions are shown in the figure). Since 5d–4f transitions are parity-allowed the decay times of d–f luminescence should lie in the nanosecond range and, in particular, the decay time of 5d–4f luminescence from Nd^{3+} in $LiKYF_5$ is 9.1 ns. However, in the case of Er^{3+} and Tm^{3+}
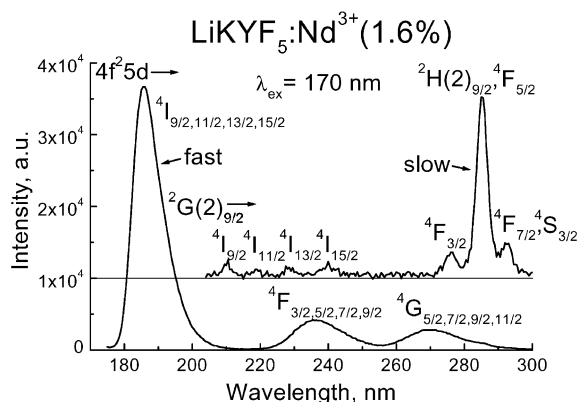

Fig. 1. Emission spectra of 5d–4f and 4f–4f luminescence from Nd^{3+} doped into a $LiKYF_5$ crystal excited by 170 nm photons at 300 K. The assignments of the bands to particular transitions are shown.

the decay kinetics of d–f luminescence is more complicated.

Recent studies of VUV emission of Er^{3+} and Tm^{3+} ions incorporated in some of fluoride crystals have shown that the emission spectrum due to interconfiguration 5d–4f transitions consists of two series of bands for either of these ions: the fast emission bands with the decay constant in the range from a few to tens of nanoseconds for different crystals and (or) slow emission bands shifted to longer wavelengths with the decay constant in the microsecond range [6,7]. As it has been established [8], the fast and slow components arise from spin-allowed (S-A) and spin-forbidden (S-F) 5d–4f transitions, respectively. This effect can be illustrated by the luminescence spectra of a BaY_2F_8 crystal doped with Er^{3+} and a TmF_3 crystal (Figs. 2 and 3). The assignments of emission bands to various 5d–4f transitions in Er^{3+} and Tm^{3+} are also shown in Figs. 2 and 3. The bands indicated in the figures correspond to the S-A 5d–4f transitions (the fast component), i.e. transitions from the low-spin emitting state of the 4f5d configuration ($2S+1=4$ for Er^{3+} and 3 for Tm^{3+}) to different energy levels of the 4f ground configuration for Er^{3+} or Tm^{3+} ions. Accordingly, the bands due to the S-F 5d–4f transitions (the slow component), i.e. transitions from the high-spin emitting state of the 4f5d
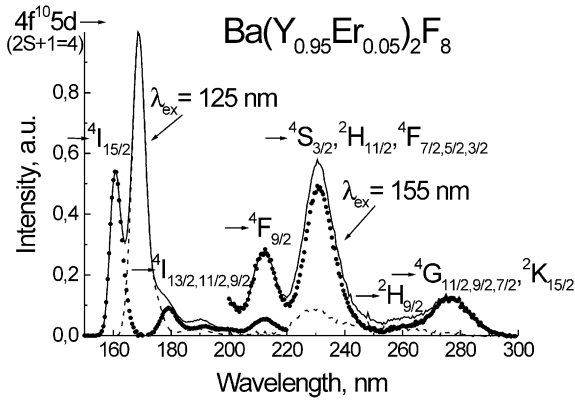
Fig. 2. Emission spectra of 5d–4f luminescence from Er^{3+} doped into a BaY_2F_8 crystal at 300 K (the dots indicate the fast component, the dashed line is the slow component and the solid line is the total intensity). The excitation wavelengths were 125 and 155 nm for different parts of the spectrum. The assignments of the bands to particular spin-allowed 5d–4f transitions are shown.
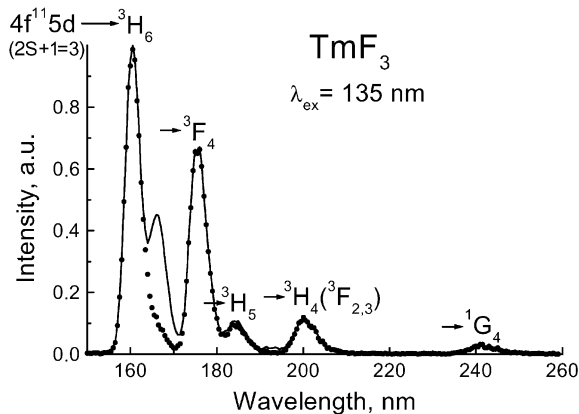

Fig. 3. Emission spectra of 5d–4f luminescence from Tm^{3+} in a TmF_3 crystal at 300 K (the dots indicate the fast component and the solid line is the total intensity). The excitation wavelength was 135 nm. The assignments of the bands to particular spin-allowed 5d–4f transitions are shown.

configuration ($2S + 1 = 6$ for Er^{3+} and 5 for Tm^{3+}) to the same energy levels of the 4f ground configuration for Er^{3+} or Tm^{3+}, are shifted to longer wavelengths.

Excitation spectra of different emissions for Er^{3+} doped into a $LiYF_4$ crystal are shown in Fig. 4. In the UV and the visible range only
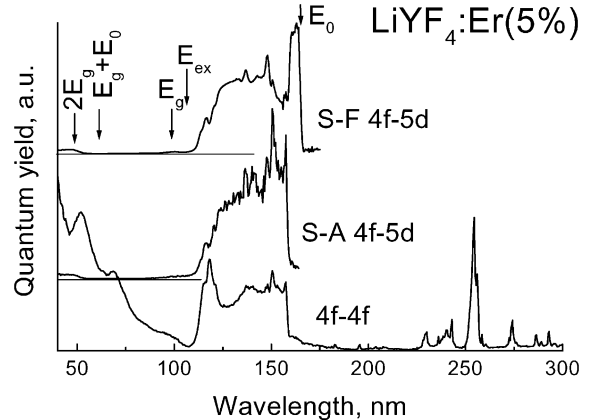

Fig. 4. Excitation spectra of the spin-allowed and the spin-forbidden 5d–4f luminescence as well as of the 4f–4f luminescence from Er^{3+} for a 5 at% Er^{3+} doped $LiYF_4$ crystal at 300 K.

narrow lines in the excitation spectrum of 4f–4f luminescence are observed. At shorter wavelengths the onset of the S-F f–d absorption is situated at ≈ 165 nm, which corresponds to the threshold of excitation for the S-F d–f microsecond luminescence. At even more shorter wavelengths the onset of the S-A f–d absorption appears at ∼ 158 nm. At these wavelengths the intensity of the S-F luminescence decreases sharply due to a higher value of the absorption coefficient for the S-A transitions. Actually, in this region the S-F luminescence is excited indirectly via the energy transfer from a higher-lying 5d level, from which the S-A transitions occur. The f–f luminescence is also excited under both the S-F and the S-A f–d absorption. When the wavelength of excitation is close to the fundamental absorption edge of the $LiYF_4$ matrix ($\lambda \sim 110$ nm) the quantum yield of both the S-A and the S-F d–f luminescence drops drastically although this is not observed in the case of the f–f luminescence. In other words, no efficient energy conversion from the matrix to d–f luminescence is observed for Er^{3+} and Tm^{3+} in both $LiYF_4$ and most of other hosts. The efficiency of energy conversion is extremely low until the energy of excitation reaches the threshold for the processes of electronic excitations multiplication. This threshold ($\lambda \sim 55$ nm) has been found to lie at photon energy less than 2 band-gap energies and

the effect is much more pronounced at higher concentrations of Er^{3+} or Tm^{3+} [9]. These features indicate clearly that the mechanism of the energy transfer from the matrix to d–f luminescence is the so-called impact mechanism of electronic excitations multiplication when fast photoelectrons in the conduction band excite directly the emission centers in the crystals.

It has been found that stoichiometric Er^{3+}-containing compounds have decay properties of d–f luminescence which are absolutely different from those of stoichiometric Tm^{3+}-containing crystals [10,11]: the decay constant of the S-F luminescence for Er^{3+} becomes as short as few nanoseconds while that for Tm^{3+} remains in the time range of hundreds of nanoseconds. This is due to the considerable difference between the energy level schemes for high-lying 4f states of Er^{3+} and Tm^{3+}. In case of Tm^{3+} no high-lying 4f levels with energies close to the energy of the lowest (emitting) 5d levels exist, while in case of Er^{3+} energy levels of some high-lying 4f states are very close to the emitting 5d levels. Therefore, the additional channels of nonradiative decay via energy transfer to neighbouring ions lead to shortening (concentration quenching) the emission for both the S-F and the S-A d–f luminescence. The effect of concentration quenching is illustrated by Fig. 5, where shortening of the decay time for the S-F luminescence with the Er^{3+} concentration is shown for a series of the $Ba(Y_{1-x}Er_x)_2F_8$ crystals.

The existence of the slow S-F 5d–4f lumines-cence as well as very low efficiency of the energy transfer from the matrix to 5d–4f luminescence make almost impossible the use of Er^{3+} and Tm^{3+} doped crystals as fast VUV scintillators. However, for Er^{3+} doped crystals the combined effect of concentration quenching and impact excitation can result in both fast decay and relatively high quantum yield of the Er^{3+} d–f luminescence in highly doped (stoichiometric) crystals. For example, at high-energy excitation in Er^{3+} doped $LiYF_4$ crystals the concentration quenching leads to the decrease of the total quantum yield of d–f luminescence, however the quantum yield of the fast S-A component ($\lambda \sim 157$ nm) increases with the Er^{3+} concentration [9]. Nevertheless,
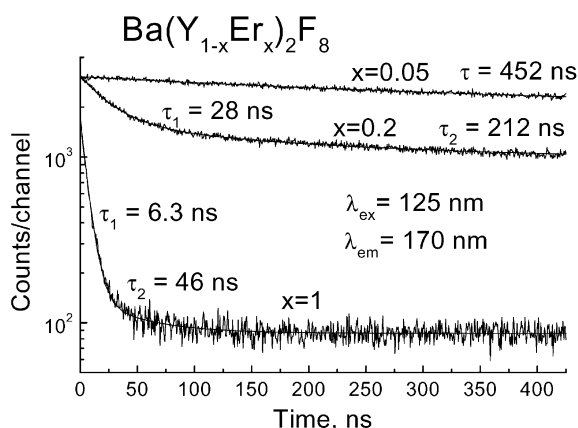

Fig. 5. Decay curves of the spin-forbidden 5d–4f luminescence from Er^{3+} in $Ba(Y_{1-x}Er_x)_2F_8$ crystals ($x = 0.05; 0.2$ and 1.0) at 300 K. The excitation wavelength was 125 nm.

none of Er^{3+} or Tm^{3+} containing fluoride crystals studied in this work has VUV light output larger than that of the well-known scintillator BaF_2.

The low light output of d–f luminescence at high energy excitation is rather general property of fluoride crystals doped with RE ions. This is due to the fact that the conventional recombination mechanism of the energy transfer is usually inefficient in such crystals. However, in most oxygen-containing matrices the recombination mechanism can be very efficient although the decay kinetics usually has a considerable fraction of the slow component. In this context, two oxygen-containing matrices doped with Nd^{3+}, namely YPO_4 and $LuPO_4$, where d–f luminescence of Nd^{3+} in the VUV (189 nm) is observed, can be mentioned [12]. The light output of the VUV emission from these materials is comparable with that of most efficient Ce^{3+} doped scintillators, but timing properties of VUV emission are quite poor to obtain a good time resolution. On the other hand, at least one fluoride crystal, K_2YF_5, doped with Nd^{3+} in which the efficient recombination mechanism of the energy transfer from the matrix to Nd^{3+} resulting in 5d–4f luminescence (185 nm) is observed has been found for the present time [11]. Besides, it is not unlikely to suppress considerably the slow component of the 5d–4f

luminescence by a proper choice of the RE ion concentration.

The competition between the S-A and the S-F luminescence of Er^{3+} or Tm^{3+} depends on the relative energy position of emitting 5d levels original for the S-A and the S-F transitions. If the energy gap between these levels is small enough (not more than 4–5 times larger than the cutoff phonon energy of the crystal), multi-phonon relaxation will exceed the rate of the radiative decay from the higher-lying 5d level responsible for the S-A transitions, which results in "pumping" the lower-lying "metastable" 5d level responsible for the S-F transitions. In other words, the energy level diagram of the 5d–4f transitions for these two ions in fluoride crystals represents a typical four-level laser scheme. Indeed, in some crystals, e.g. KYF_4, the intensity of the S-A luminescence of Er^{3+} or Tm^{3+} is extremely weak [13], i.e. in such crystals there exists very efficient nonradiative relaxation from higher-lying 5d states to the lowest 5d level responsible for the S-F luminescence. This peculiarity results in a larger Stokes shift of 5d–4f luminescence from the edge of the strong S-A 4f–5d absorption for Er^{3+} and Tm^{3+} than for Nd^{3+}, i.e. to a smaller re-absorption of emitted radiation by such crystals. Relatively wide emission bands due to 5d–4f transitions in these ions (for example, in a KYF_4 crystal the FWHM is 4.6 and 6.5 nm for Er^{3+} and Tm^{3+}, respectively) offer a possibility for tunable laser design. Obviously, one can expect that optical pumping, for example from a noble-gas discharge, will be very efficient in the wide spectral range of strong 4f–5d absorption.

4. Conclusions

It has been shown that many fluoride crystals doped with Nd^{3+}, Er^{3+} or Tm^{3+} have intense VUV luminescence due to interconfiguration 5d–4f transitions in the RE ions. Strong concentration quenching, which leads to nanosecond decay of the S-F 5d–4f luminescence from Er^{3+}, has been found in crystals highly doped with Er^{3+}. Due to this feature the decay properties of VUV lumines-cence from Er^{3+} and Tm^{3+} in highly doped fluoride crystals are absolutely different.

Neither Er^{3+}- nor Tm^{3+}-containing materials studied in this work have shown better scintillation properties than those of the well-known scintilla-tor BaF_2 for the use as fast VUV scintillators. Only some Nd^{3+} doped crystals have simultaneously both high light output and relatively good timing properties of VUV luminescence.

The S-A 5d–4f luminescence of Er^{3+} or Tm^{3+} doped into some crystals is extremely weak, i.e. in such crystals there exists very efficient nonradiative relaxation from higher-lying 5d states to the lowest 5d level responsible for the S-F luminescence. This peculiarity of the studied crystals doped with Er^{3+} or Tm^{3+} can be very attractive for developing VUV solid state lasers based on crystals of such a type.

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