Crystal Growth and Spectroscopic Investigation of Yb$^{2+}$-Doped Fluoride Crystals

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Received July 16, 2000

Abstract—In this presentation we report on the preparation and spectroscopic properties of Yb$^{2+}$-doped MgF$_2$, KMgF$_3$, LiCaAlF$_6$, and LiSrAlF$_6$ with respect to the realization of a tunable solid state laser based on a interconfigurational transition of Yb$^{2+}$. All materials exhibit broadband emission in the short-wavelength region due to a 5d–4f transition. The peak emission wavelengths and bandwidths at room temperature are in particular 485 nm and 4510 cm$^{-1}$ for Yb$^{2+}$: MgF$_2$, 400 nm and 3890 cm$^{-1}$ for Yb$^{2+}$: KMgF$_3$, 393 nm and 3260 cm$^{-1}$ for Yb$^{2+}$: LiCaAlF$_6$, 440 nm and 5180 cm$^{-1}$ for Yb$^{2+}$: LiCaAlF$_6$, respectively. The emission can be excited in the energy level of the 4f$^{13}5d$ configuration. An energy level scheme for Yb$^{2+}$: MgF$_2$ in the strong field assignment is proposed. The room temperature decay time of the Yb$^{2+}$ emission is 52 μs in MgF$_2$, 80 μs in KMgF$_3$, 5.4 μs in LiCaAlF$_6$ and 9.9 μs in LiSrAlF$_6$, respectively.

INTRODUCTION

Lasers in the UV and visible spectral range can be used in a wide field of applications such as biology, medicine, display technology, data storage, printing industry, scientific research, and entertainment. One possible way to obtain laser oscillation in this spectral range is the exploitation of the parity allowed (and thus electric-dipole allowed) 4f–5d transitions of divalent and trivalent rare earth ions, such as, e.g., Ce$^{3+}$ [1]. In this presentation, we report on the preparation and spectroscopic investigation of the Yb$^{2+}$ ion. Yb$^{2+}$ has a completely filled 4f shell, therefore there are no inner-shell 4f–4f transitions. The observed transitions are thus assigned to interconfigurational transitions. First investigations of Yb$^{2+}$ were performed in alkaline earth halides, alkali halides, and recently in fluorides and oxides [2]. Here, preparational aspects and laser relevant spectroscopic data on Yb$^{2+}$-doped MgF$_2$, KMgF$_3$, LiCaAlF$_6$ (LiCAF), and LiSrAlF$_6$ (LiSAF) will be presented. Detailed spectroscopic data on Yb$^{2+}$: MgF$_2$ and Yb$^{2+}$: KMgF$_3$ can be found in [2, 3].

CRYSTAL GROWTH

All crystals were grown from stoichiometric melts by the Czochralski method using RF-heating, carbon crucibles and automatic diameter control. Single crystals were grown with a pulling rate of 1 mm/h in good optical quality and diameters up to 14 mm. The starting materials were premelted under HF atmosphere to avoid traces of oxygen and water. LiSAF, LiCAF, and MgF$_2$ contain a suitable divalent cation site, so a reducing atmosphere (N$_2$ + 5% H$_2$) during the growth was sufficient to stabilize the divalent state of Yb. In KMgF$_3$ the Yb$^{2+}$ ion occupies the monovalent K$^+$ site. Therefore charge compensation was utilized by codoping with lithium. Some properties of the crystals investigated are summarized in Table 1.

EXPERIMENTAL SETUP

The absorption spectra are measured with a commercial Cary 2400 photospectrometer. The excitation and emission spectra for the wavelength region above 250 nm were obtained with a Spex Fluorolog 3 system. For the excitation measurements between 130 and 250 nm the SUPERLUMI setup at the Hamburger Synchrotronstrahlungslabor (HASYLAB) was used. For details of this VUV setup see [4]. For the lifetime measurements, a Q-switched frequency-tripled flash lamp pumped Nd : YAG laser (Spectra-Physics Quanta-Ray GCR-130) with a pulse duration of 6ns was used.

SPECTROSCOPIC RESULTS AND DISCUSSION

The room temperature absorption, excitation, and emission spectra of Yb$^{2+}$-doped MgF$_2$, KMgF$_3$, LiCAF, and LiSAF are shown in Fig. 1. The excitation bands are in good agreement with the absorption bands. All observed absorption and excitation bands are assigned to 4f–5d transitions of the Yb$^{2+}$-ion. The absorption cross section of the lowest absorption band is in the order of 1 × 10$^{-18}$ cm$^2$, which is a typical value for a parity allowed transition. The room temperature lifetimes...
are 52 μs for MgF₂, 80 μs for KMgF₃ [3], 9.9 μs for LiSAF, and 5.4 μs for LiCAF. Using these lifetimes and assuming a quantum efficiency of 100% at room temperature, an upper limit for the emission cross section can be determined with the formula of McCumber [5]:

$$\sigma_{em} = \eta \frac{1}{\sqrt{4\pi c n^2}} \frac{\lambda^4}{\tau \Delta \lambda},$$

where $\eta$ is the quantum efficiency, $c$ is the speed of light, $n$ is the refractive index, $\tau$ is the emission lifetime, $\lambda$ is the peak emission wavelength, and $\Delta \lambda$ is the emission bandwidth. For all crystals investigated $\sigma_{em}$ is determined to be between $0.3 \times 10^{-20}$ cm$^2$ and $5.6 \times 10^{-20}$ cm$^2$, which is a rather low value for a parity allowed transition and much smaller than the absorption cross section. The spectroscopic data are summarized in Table 2.

**DISCUSSION**

The ground configuration of the Yb$^{2+}$-ion is $4f^{14}$. This completely filled shell leads to a $^1S_0$ ground state of the free ion. In an octahedral crystal field, this state transforms like the $^1A_1$ irreducible representation. No other $4f$ levels exist. The excited $4f^{13}5d$ configuration consists in total of 140 energy levels. For the interpretation of the observed excitation spectra, it is instructive to use the strong-field-assignment by Loh [6, 7]. The $5d$ electron splits in a crystal field into a threefold degenerated $t_2$ and a twofold degenerated $e$ level. In an octahedral coordination of the Yb$^{2+}$-ion, the $t_2$ level is lower, in a tetrahedral or cubic coordination the $e$ level is lower. The splitting between the $t_2$ and $e$ level is per definition $\Delta = 10Dq$. In lower symmetry crystal fields, these levels split further. The $4f^{13}$-core is considered in the same way as for an Yb$^{3+}$-ion, with the two manifolds $^2F_{7/2}$ and $^2F_{5/2}$ separated by about $\Delta E_{4f} \approx$

![Figure 1. Room temperature absorption, emission, and excitation spectra of Yb$^{2+}$-doped MgF₂, LiSrAlF₆, LiCaAlF₆, and KMgF₃. The excitation spectra were measured in different setups and combined.](image-url)
The spin of the 5d electron can be parallel or antiparallel to that of the 4f13-core; thus, the whole energy level scheme exists for singlet and for triplet states, from which the triplet states are energetically lower. The transitions to the triplet states are spin-forbidden, thus in the excitation and absorption spectra mainly the transitions to the singlet levels are observed.

In Fig. 2 the energy level scheme obtained from the strong field assignment of Yb2+ in MgF2 (D2h site symmetry) is shown. In Table 3 the measured values for the observed excitation bands are listed. From these data, the splittings due to the different configurations (Δconf = 43214 cm−1), due to the 5d electron in an Oh crystal field (Δ = 22192 cm−1), due to the LS-coupling of the 4f13-core of Yb3+ (ΔE4f = 9000–11000 cm−1) and due to the lowering of the crystal field symmetry to D2h (ΔECF = 1950–3850 cm−1) are determined. The obtained results are in reasonable agreement with the expected values for the corresponding energy level splittings. However, for a detailed calculation of the energy levels, the Coulomb interaction between the 5d electron and the 4f13-core has to be taken into account.

The lifetimes are rather long for a parity allowed transition, especially at low temperatures, where they are in the order of several ms, see Table 2. The possible reason is, that the lowest 4f135d level is a triplet state, thus the emission is spin-forbidden. Lizzo et al. [2, 3] explained the long lifetime also with a small overlap between the wavefunctions of the hole in the contracted 4f-orbital and of the delocalized 5d electron. Kaplyanskii et al. [8] also considered the possibility, that the metastable level could be a 4f136s state. In this case the emission would require Δl = 3 and would therefore be strongly forbidden.
First laser tests with Yb\textsuperscript{2+}-doped MgF\textsubscript{2} were not successful. In the experiments, there were hints for excited state absorption at the pump wavelength of 355 nm. Further measurements of the excited state absorption are in progress.

**SUMMARY AND CONCLUSION**

Yb\textsuperscript{2+}-doped MgF\textsubscript{2}, KMgF\textsubscript{3}, LiCaAlF\textsubscript{6}, LiSrAlF\textsubscript{6} crystals were successfully grown by the Czochralski method. The observed absorption and excitation bands are assigned to 4f–5d transitions of the Yb\textsuperscript{2+}-ion. An energy level scheme for Yb\textsuperscript{2+} : MgF\textsubscript{2} in the strong field assignment was developed. The observed long lifetime of the emission is thus far not understood. Laser oscillation was not obtained yet, probably due to excited state absorption.

**ACKNOWLEDGMENTS**

This work was supported by the Deutsche Forschungsgemeinschaft within the frame of the Graduierten-Kolleg no. 463. Parts of the measurements were performed at the SUPERLUMI station of the Hamburger Synchrotronstrahlungslabor (HASYLAB) within the frame of project II-99-065.

**REFERENCES**