



ELSEVIER

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Vacuum ultraviolet synchrotron measurements of excitons in NaMgF₃:Yb²⁺

Rosa B. Hughes-Currie^a, Konstantin V. Ivanovskikh^{c,d}, Michael F. Reid^{a,b,*}, Jon-Paul R. Wells^{a,f}, Roger J. Reeves^{a,b}, Andries Meijerink^e

^a Department of Physics and Astronomy, University of Canterbury, PB 4800, Christchurch 8140, New Zealand

^b MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand

^c ANK Service Ltd., PB 58, Novouralsk 624131, Sverdlovsk Region, Russia

^d Ural Federal University, 19 Mira st., Ekaterinburg 620002, Russia

^e Debye Institute, Utrecht University, P.O. Box 80 000, 3508 TA Utrecht, Netherlands

^f Dodd-Walls Centre for Quantum and Photonic Technologies, New Zealand

ARTICLE INFO

Article history:

Received 16 September 2014

Received in revised form

5 March 2015

Accepted 19 March 2015

Available online 26 March 2015

Keywords:

Self-trapped exciton

Impurity-trapped exciton

Lanthanide

Ytterbium

NaMgF₃

VUV spectroscopy

ABSTRACT

Results of a vacuum ultraviolet spectroscopic characterization of NaMgF₃:Yb²⁺ are presented. The material demonstrates emission features associated with self-trapped excitons and impurity-trapped excitons. The emission features noticeably overlap giving rise to a broad emission band from 17 000 to 35 000 cm⁻¹ at a sample temperature of 8 K. To identify the true profiles of the emission features we have used a deconvolution procedure. The deconvolution was possible due to the thermal quenching of self-trapped excitons at room temperature that allowed for direct observations of the impurity trapped exciton emission band. Energy transfer between host electronic excitations (excitons and e–h pairs) and Yb²⁺ ions leading to the formation of impurity-trapped excitons is evident from excitation spectra.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

NaMgF₃ has been investigated as a host material for dosimetry as its effective atomic number is similar to human tissue. Due to its luminescence properties when doped with certain rare-earth ions NaMgF₃ can be used as a material for optically stimulated luminescence (OSL) dosimetry, a versatile alternative to thermoluminescence (TL) dosimetry. OSL measurements have been performed on NaMgF₃ doped with divalent europium [1] and trivalent cerium [2].

Finding new materials for applications such as OSL dosimetry is aided by greater understanding of the nature of the phenomena which lead to luminescence in the materials. Studying luminescence properties of materials upon excitation near or above the band edge allows insight into the energy transfer processes between NaMgF₃ excited states and luminescent impurity centers. In this study we present results of VUV spectroscopic study of NaMgF₃ doped with Yb²⁺. This material provides an interesting model for understanding

relaxation processes leading to the formation of impurity-trapped excitons (ITE) via relaxation of host excitons on Yb²⁺ ions.

When NaMgF₃:Yb²⁺ is excited into its 4f¹³5d configuration, its emission is a very broad band with a large Stokes shift indicating that the emission is from an ITE [3]. ITEs are formed when a 5d electron becomes delocalized over surrounding cations. Because an electron has been ionized, there is a hole in the Yb²⁺ valence band and the combination of the hole and Yb²⁺ ion can be represented as a Yb³⁺ ion. A long range Coulomb interaction that attracts the ionised electron to the Yb³⁺ ion makes the center effectively Yb³⁺ + e⁻. In most materials used in practical applications, the ITEs form and relax as part of a non-radiative process and cannot be detected. NaMgF₃:Yb²⁺ is one of the few materials where the ITE energy levels are below the luminescent states of the rare earth ion and the ITEs have direct radiative recombination [4].

Free excitons in NaMgF₃ self-trap and radiatively recombine producing a visible self-trapped exciton (STE) emission band from 17 000 to 35 000 cm⁻¹ [5]. The structure of the STE in NaMgF₃ lacks detailed investigation. Some spectroscopic and dynamic characteristics of the STEs have been studied in fluorides with formula XMgF₃ (where X is Na, K, or Rb) [6]. The configuration of

* Corresponding author at: Department of Physics and Astronomy, University of Canterbury, PB 4800, Christchurch 8140, New Zealand.

E-mail address: mike.reid@canterbury.ac.nz (M.F. Reid).

the STE in KMgF_3 is expected to be similar to that in NaMgF_3 and has been studied with EPR [7] and extended-ion calculations [8].

This paper aims at better understanding of spectroscopic and dynamic properties of excitonic formations, both STE and ITE, in $\text{NaMgF}_3:\text{Yb}$ single crystals. We present and discuss the emission subsequent to excitation into the $\text{Yb}^{2+} 4f^{13}5d$ states and also high energy excitation around the band edge. Evidence of energy transfer from the intrinsic excitons to the ITE is presented and discussed.

2. Experimental details

The crystal used in this experiment contained 0.6 mol% of ytterbium and was grown using the Bridgman technique in a reducing atmosphere. The VUV spectroscopic measurements were carried out using the SUPERLUMI facility at HASYLAB of DESY (Hamburg, Germany). The setup allows UV-VUV spectroscopic measurements with synchrotron radiation [9]. Synchrotron radiation (SR) from the DORIS III storage ring was the excitation source. For excitation measurements in the range of 3.7–21 eV a 2 m monochromator in McPherson mounting with a resolution of 3.2 Å was used. The detection of the luminescence was performed with a 0.3 m ARC SpectraPro-308i monochromator equipped with a high-speed R3809U-50S (Hamamatsu) microchannel plate (MCP) detector. The spectra were recorded counting emission signal within the whole time period of 480 ns available between SR pulses at a 2 bunch mode (BM) of the storage ring. The measurements were performed in the temperature range of 8–300 K in the ultra-high-vacuum chamber (approximately 10^{-9} mbar). The excitation spectra were corrected for the wavelength-dependent variation of the SR intensity using a sodium salicylate signal. A background signal corresponding to the dark count of the MCP detector was subtracted from the spectra.

3. Results

Fig. 1 shows the 8 K excitation spectra monitoring at the ITE and STE emission peaks shown in Fig. 2. As indicated in the figure, emission from the ITE is observed upon excitation into the $4f^{13}5d$ states of the Yb^{2+} ion as well as the host excitonic states. Meanwhile, the STE emission can only be excited via formation of free excitons or

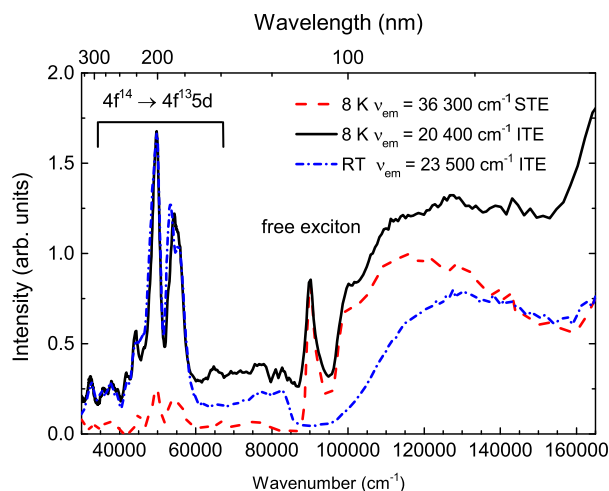


Fig. 1. Excitation spectra of $\text{NaMgF}_3:0.6\%\text{Yb}^{2+}$ at a sample temperature of 8 K. At 20 400 cm^{-1} detection the emission is mostly from ITEs, and at 36 300 cm^{-1} the emission is mostly from STEs. The blue dotted line is the excitation spectrum at a sample temperature of 300 K monitoring the ITE emission at 23 500 cm^{-1} . (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

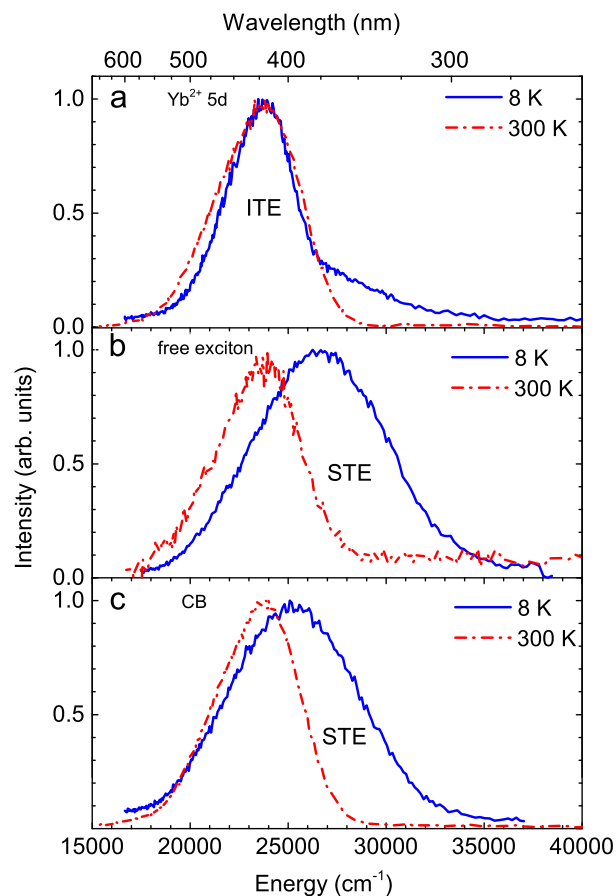


Fig. 2. Emission from $\text{NaMgF}_3:0.6\%\text{Yb}^{2+}$ at a sample temperature of 8 K and 300 K. (a) Below bandgap excitation into a $\text{Yb}^{2+} 5d$ level at 54 600 cm^{-1} for 8 K and 49 800 cm^{-1} for 300 K. (b) Excitation into the free exciton peak at 90 100 cm^{-1} for 8 K and 87 000 cm^{-1} for 300 K. (c) Above band gap excitation at 118 000 cm^{-1} for both temperatures.

upon higher energy excitation that corresponds to generation of separated electron–hole pairs. The peak at 90 000 cm^{-1} is the free exciton peak. This peak is reported in reflectance measurements [10].

Energy transfer between intrinsic excitons and Yb^{2+} ions is evident from the presence of the excitonic peak observed at 90 000 cm^{-1} when ITE emission is monitored. The most likely path from the formation of free excitons to ITE emission is formation of STEs and energy transfer from the STEs to Yb ions. Energy transfer from STEs to luminescent centres has been shown in other materials [11,12]. A schematic of this process is shown in our previous paper on VUV spectroscopy of $\text{CaF}_2:\text{Yb}^{2+}$ [13].

The emission shifts with changing excitation energy in Fig. 2. In Fig. 2(a) the system is excited into a 5d state below the bandgap and the emission is at 19 000–27 000 cm^{-1} , previously identified as ITE emission [3]. In Fig. 2(b) excitation into the free exciton peak results in a broadening and shift of emission towards a higher energy compared to the emission following excitation into a 5d state. The emission energy shift between Fig. 2(a) and (b) occurs because in (b) the emission is predominantly from radiative recombination of

Table 1

The approximate normalised areas of Gaussian functions simulating the peaks of the ITE and STE emission bands deconvoluted from the 8 K spectra in Fig. 2(b) and (c).

Excitation region	ITE emission	STE emission
Excitation into free exciton	0.20	0.80
Band-to-band excitation	0.32	0.68

NaMgF₃ STEs [5] rather than ITEs. When the crystal is excited at 118 000 cm⁻¹ in Fig. 2(c) the emission is similar to Fig. 2(b) but the peak of the emission band is shifted to a slightly lower energy.

Fig. 2 shows how the interplay between ITE and STE emission can be observed with changing excitation energy and temperature. Upon excitation into a Yb²⁺ excited state the emission is all from the Yb ITE. Upon excitation in the range of fundamental absorption (the free exciton and higher energies) the emission shifts to lower energy at high temperature because the STE emission is quenched.

To deconvolve the two emission bands from each other we can model the 8 K spectrum with two Gaussian functions. Since the 300 K data is predominantly ITE emission we can first fit the 300 K data to a Gaussian function. Then we scale this Gaussian function and add it to another Gaussian function at a higher energy, representing the STE emission.

We can estimate the total intensity of the emission from the ITE compared to the STE by taking the ratio of the areas under the two Gaussian functions. The normalised areas of these Gaussians are given in Table 1. When the excitation is into the free exciton peak, there is approximately a quarter as much emission from ITE states as STE states. When the excitation is a band-to-band transition, there is about half as much. This relative increase in the ITE emission indicates that upon a band-to-band excitation there is a mechanism for populating radiating ITE states which is independent from populating STE states. This ITE formation occurs via the same pathway for energy transfer from the conduction band to the ITE shown in the 300 K excitation spectrum in Fig. 1. Upon room temperature excitation into the free exciton, no ITE emission is observed which suggests that ITE formation at 300 K must be either by excitation into 5d levels or energy transfer from the conduction band.

4. Conclusion

VUV excitation measurements of NaMgF₃:Yb²⁺ spanning a broad spectral range of 35 000–160 000 cm⁻¹ have been carried

out. When the crystal was excited at an energy to optimally create free excitons, emission bands due to both ITE and STE states are observed, suggesting that the free excitons become trapped as STEs, which then go on to relax radiatively or excite Yb²⁺ ions. By modeling the emission bands as Gaussian functions, we have found the emission from the ITE approximately doubles in comparison to STE emission as the excitation energy is increased from the intrinsic exciton resonance peak to a band-to-band transition. This is evidence that emitting ITE states are also created through energy transfer from electron-hole pairs, which is also shown in room temperature excitation measurements.

Acknowledgements

This work was supported by the Marsden fund of the Royal Society of New Zealand via Grant 09-UOC-080. The measurements were carried out at the SUPERLUMI station of the Hamburg HASYLAB facility. R.B.H.C. acknowledges support from the University of Canterbury. K.V.I. acknowledges partial support of the Ural Federal University via the UrFU Competitiveness Enhancement Program.

References

- [1] C. Dotzler, G. Williams, U. Rieser, A. Edgar, *Appl. Phys. Lett.* **91** (2007) 121910.
- [2] N. Le Masson, A. Box, C. Van Eijk, C. Furetta, J.-P. Chaminade, *Radiat. Prot. Dosim.* **100** (2002) 229–234.
- [3] S. Lizzo, A. Meijerink, G. Dirksen, G. Blasse, *J. Phys. Chem. Solids* **56** (1995) 959–964.
- [4] P. Dorenbos, *J. Phys.: Condens. Matter* **15** (2003) 2645.
- [5] E. Van der Kolk, P. Dorenbos, C. Van Eijk, A. Vink, M. Weil, J.-P. Chaminade, *J. Appl. Phys.* **95** (2004) 7867–7872.
- [6] A. Voloshinovskii, V. Mikhailik, P. Rodnyi, *Radiat. Eff. Defects Solids* **135** (1995) 281–283.
- [7] W. Hayes, I. Owen, G. Pilipenko, *J. Phys. C: Solid State Phys.* **8** (1975) L407.
- [8] G. Huang, L. Chen, M. Liu, D. Xing, *J. Phys.: Condens. Matter* **15** (2003) 4567.
- [9] G. Zimmerer, *Radiat. Meas.* **42** (2007) 859–864.
- [10] H. Takahashi, R. Onaka, *J. Phys. Soc. Jpn.* **43** (1977) 2021–2029.
- [11] A. Belsky, I. Kamenskikh, V. Mikhailik, C. Pedrini, A. Vasil'Ev, *Radiat. Eff. Defects Solids* **150** (1999) 1–10.
- [12] Y. Zhou, S. Feofilov, H. Seo, J. Jeong, D. Keszlner, R. Meltzer, *Phys. Rev. B* **77** (2008) 075129.
- [13] R. Hughes-Currie, A. Salkeld, K. Ivanovskikh, M. Reid, J.-P. Wells, R. Reeves, *J. Lumin.* **158** (2015) 197–202.
- [14] R. Williams, K. Song, *J. Phys. Chem. Solids* **51** (1990) 679–716.