J Mater Sci (2010) 45:1469–1472
DOI 10.1007/s10853-009-4104-5

Luminescence properties and electronic structure of Sm^{3+}-doped $YAl_3B_4O_{12}$

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Received: 17 June 2009 / Accepted: 2 December 2009 / Published online: 22 December 2009

Abstract The luminescence properties of Sm^{3+} ions in $YAl_3B_4O_{12}$ were studied upon synchrotron excitation in the 3.8–11 eV region. In addition to the $4f \rightarrow 4f$ excitation bands, the excitation spectra of the Sm^{3+} emission contain broad bands at 6.1 and ~7.0 eV. These bands are attributed to charge transfer transition in Sm^{3+}–O^{2-} complexes and $4f \rightarrow 5d$ transition of Sm^{3+} ions, respectively. The optical absorption edge of $YAl_3B_4O_{12}$ was determined at 7.3 eV. A comparison with the results of electronic structure calculations on $YAl_3B_4O_{12}$ is also made.

Introduction

Crystals of lanthanide (Ln^{3+})-doped yttrium–aluminum borate, $YAl_3B_4O_{12}$, are of great interest due to their applications as active laser media and nonlinear optical materials for laser frequency conversion [1–3]. $YAl_3B_4O_{12}$ is isostructural with the mineral huntite, and in this structure yttrium ions are coordinated by six oxygen ions, which form a trigonal prism. The point symmetry for the Y^{3+} ions is D_3. The most prominent structural feature of $YAl_3B_4O_{12}$ is that the Y^{3+} ions are separated from each other by aluminum octahedra and isolated BO^{3-} groups, so that the minimal distance (R_0) between Y^{3+} ions is large ($R_0 \approx 5.9$ Å) [4, 5]. Several groups of authors have reported the luminescence properties of lanthanide ions (including Sm^{3+}) in $YAl_3B_4O_{12}$ upon excitation in ultraviolet–visible range [6–10]. It was found that the emission spectrum of Sm^{3+} ions in $YAl_3B_4O_{12}$ consists mainly of four groups of lines in the 550–720 nm region, due to the transitions from the $^4G_{5/2}$ level to the levels $^6H_{5/2,7/2,9/2,11/2}$. The most intense group of lines is caused by the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition ($\lambda_{max} = 599$ nm). The $YAl_3B_4O_{12}$ crystals were also used as interesting model systems to study energy transfer processes between lanthanides ions [6, 9, 10]. The concentration quenching of the Sm^{3+} and Dy^{3+} emissions was attributed to resonant cross-relaxation processes. In particularly, it was found that the interaction Sm^{3+}–Sm^{3+} is preferably of the electric dipole-quadrupole type and the microparameter of the elementary interaction (C_{da}) was found to be $(3.1 \pm 0.6) \times 10^{-4}$ $nm^8/\mu s$ [9]. This value is close to those reported in the literature for Sm^{3+} ions in KYP_4O_{12} single crystals, borate, and phosphate glasses. In this work, we have studied the luminescence properties of Sm^{3+}-doped $YAl_3B_4O_{12}$ upon excitation in the vacuum ultraviolet (VUV) spectral region. A comparison with the results of electronic structure calculations on $YAl_3B_4O_{12}$ was also made.

Experimental

The undoped and Sm^{3+}-doped $YAl_3B_4O_{12}$ were synthesized in the form of polycrystalline powders. The nominal concentration of Sm^{3+} ions in the sample was 1 at%. Since the concentration quenching of the Sm^{3+} luminescence in $YAl_3B_4O_{12}$ starts at concentrations of 2–3 at% [6, 9], no processes related with concentration quenching of the

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Sm^{3+} emission are expected to occur in the sample studied in this work. The first step in the preparation involved the formation of Y_2O_3 and Y_2O_3:Sm^{3+}. To this end, hydrous yttrium (samarium) oxalate was obtained by dissolving the appropriate amounts of Y_2O_3 (99.99%) and Sm_2O_3 (99.99%) in a dilute HNO_3 solution. The $Y_2(C_2O_4)_3 \cdot 4H_2O$ was precipitated from the hot solution (about 80 °C) by the slow addition of a concentrated $H_2C_2O_4$ solution. The precipitate was then heated at 900 °C for 1 h in air to form Y_2O_3. After that the appropriate amounts of Y_2O_3 (Y_2O_3:Sm^{3+}), $Al(OH)_3$ and H_3BO_3 (15% excess) were grinded and thoroughly mixed, and the resulting mixtures were fired at a temperature of about 1150 °C for 2 h in air. The as-prepared samples were checked by X-ray diffraction (XRD) using CuK_α radiation. No impurity phases were detected in the XRD patterns. The emission and excitation spectra were recorded at 293 K using a Horiba Jobin-Ivon Fluorolog-3 spectrofluorometer equipped with a xenon lamp. For the decay time measurements, a flash xenon lamp and a pulsed YAG:Nd^{3+} laser ($\lambda_{exc} = 532$ nm) were employed. The measurements of excitation spectra at wavelengths shorter than 240 nm and emission spectra were also performed at 9 K and room temperature using synchrotron radiation and the equipment of the SUPERLUMI experimental station [11] of HASYLAB at the DESY synchrotron (Hamburg, Germany). The synchrotron operated in multi-bunch mode with bunches separated by 200 ns. These spectra were corrected for the wavelength dependent excitation intensity with the use of sodium salicylate as a standard.

Results and discussion

Since the luminescent properties of the samples at 9 and 293 K were found to be practically the same, we will report here mainly the results of low temperature measurements. The emission spectrum of undoped $YAl_3B_4O_{12}$ at 9 K is presented in the inset of Fig. 1. Upon excitation at $\lambda_{exc} = 160$ nm the emission extends from 250 to 500 nm. It has a maximum at 329 nm (3.77 eV) and a shoulder at about 385 nm (3.22 eV). Figure 1 shows the excitation spectra for the emission of $YAl_3B_4O_{12}$ at 340 nm recorded for three different time intervals after picosecond pulse excitation. The time-integrated excitation spectrum (curve a) consists of a band with a sharp edge on the lower energy side and a maximum at about 162 nm (~7.65 eV). The short-time and time-delayed excitation spectra have the same structure. A clear threshold is observed at 7.3 eV. Its position is labeled as E_{edge} in Fig. 1. This is attributed to the onset of host lattice absorption of $YAl_3B_4O_{12}$. Note that in the 7–12 eV range the excitation spectrum is similar to those for $YAl_3B_4O_{12}$ doped with either Ce^{3+} or Gd^{3+} ions [12, 13]. It is clear that the emission bands around 329 and 385 nm are an intrinsic property of $YAl_3B_4O_{12}$. Several explanations can be put forward to interpret these bands. The large Stokes shifts (>3.8 eV) of these emissions, the asymmetrical shape of the bands in their excitation spectra indicate that these features may result from self-trapped excitons [12, 14]. Note that similar emissions have been reported before for lithium borates LiB_3O_5 and $Li_2B_4O_7$. It was found that the emission of LiB_3O_5 and $Li_2B_4O_7$ with a maximum at about 345 nm is due to radiative annihilation of the self-trapped excitons [14]. Another explanation is that the emission bands at 329 and 385 nm are caused by electron-hole recombination processes with the participation of intrinsic defects of $YAl_3B_4O_{12}$. A detailed analysis of the nature of these emissions is beyond the scope of this work.

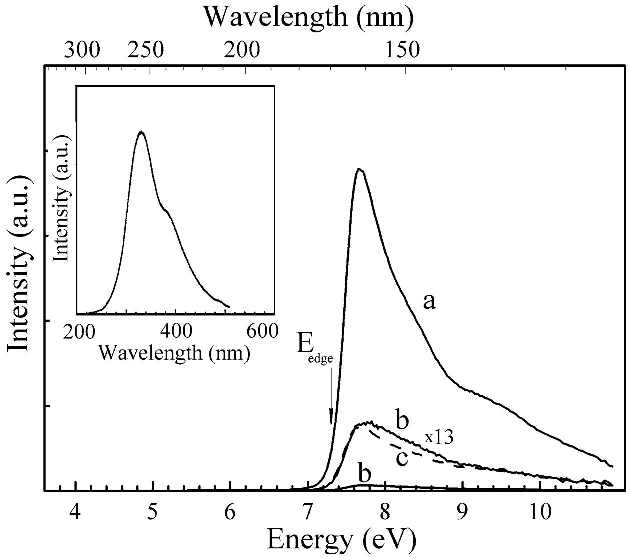

Fig. 1 VUV excitation spectra of undoped $YAl_3B_4O_{12}$ monitoring the emission at 340 nm ($T = 9$ K). The spectra were recorded for three different time intervals after picosecond pulse excitation: (*a*) between 1.5 and 180 ns, (*b*) between 1.5–6.5 ns, (*c*) between 90–180 ns. The *inset* shows the emission spectrum upon excitation at 160 nm

It was found that the introduction of Sm^{3+} ions into $YAl_3B_4O_{12}$ suppresses the intrinsic emission, but not completely. Figure 2 shows the emission and (V)UV excitation spectra of Sm^{3+} ions in $YAl_3B_4O_{12}$ at 9 K. The emission spectrum consists of four groups of lines in the 550–720 nm range. It is clear that these emission features are caused by the $^4G_{5/2} \rightarrow {}^6H_j$ transitions of Sm^{3+}. Upon direct excitation of the Sm^{3+} ions in the 280–540 nm range, the decay of the Sm^{3+} emission at 293 K was found to be single exponential with a time constant of 1.7 ± .0.1 ms. The excitation spectra of the Sm^{3+} emission in $YAl_3B_4O_{12}$ recorded for different time intervals after picosecond pulse excitation appeared to be identical,

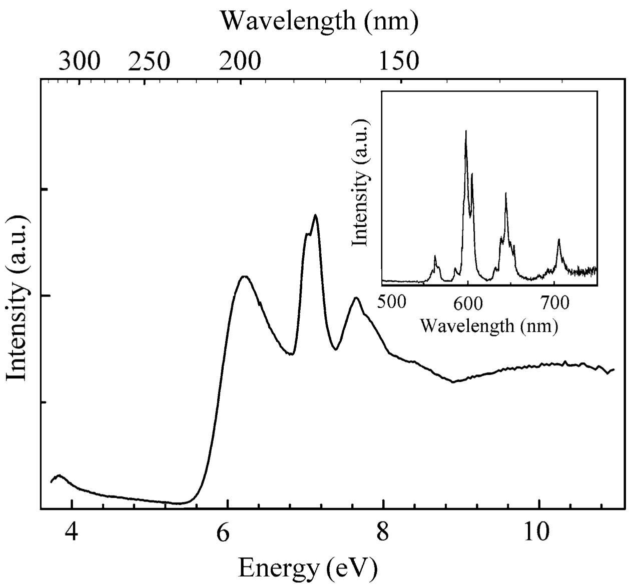

Fig. 2 Time-integrated excitation spectrum of $YAl_3B_4O_{12}$:Sm^{3+} monitoring the Sm^{3+} emission ($\lambda_{em} = 600$ nm) at 9 K. The *inset* shows the emission spectrum of Sm^{3+} ions upon excitation at 160 nm

consisting of the following features: weak bands at 321 and 275 nm caused by $4f \rightarrow 4f$ transitions of Sm^{3+}; a broad band with a maximum at about 200 nm (6.2 eV); an intense band with local maxima at 174 nm (7.12 eV) and 177 nm (7.0 eV); and a band starting at 170 nm (7.29 eV) and peaking at 162 nm (~ 7.65 eV), which is also observed in the excitation spectra of the intrinsic emission of $YAl_3B_4O_{12}$. As mentioned above, this band can be attributed to the host lattice absorption.

It is reasonable to assume that the intense band in the range 180–230 nm is caused by the charge transfer (CT) transition from the oxygen 2*p* states to the empty states of the Sm^{3+} $4f^5$-configuration. If so, the observed maximum of the Sm^{3+} CT band ($\lambda_{max} = 200$ nm) lies between the values of λ_{max} for Eu^{3+} (246 nm) [15] and Dy^{3+} ions (172 nm) [16] in this compound. This interpretation is also supported by the fact that the maximum of the Sm^{3+} CT band in $YAl_3B_4O_{12}$ is shifted to higher energies by 9350 cm^{-1} relative to the maximum of the Eu^{3+} CT band in this compound. This value of the shift agrees well with the literature data for Sm^{3+} ions in other inorganic compounds [17, 18]. Information on the $4f \rightarrow 5d$ transitions of Sm^{3+} ions is restricted to a few fluorides (CaF_2, $LiYF_4$) and YPO_4 [19, 20]. Van Pieterson et al. [20] reported that the excitation spectrum of Sm^{3+} emission in YPO_4 contains three $4f \rightarrow 5d$ bands at about 175, 153, and 147 nm. It is well known that the depression of the 5*d* level (ΔLn^{3+}) in a crystal is approximately constant along the lanthanide series [19, 21]. Dorenbos [19] found this depression to be the same for all the Ln^{3+} ions, within 600 cm^{-1}. This allows one to estimate the energy position of the 5*d* states of any lanthanide ion. By choosing *E* (Ce^{3+}, free) = 49740 cm^{-1} and *E* (Sm^{3+}, free) = 74400 cm^{-1} [22] and taking into account that for $YAl_3B_4O_{12}$ $\Delta Ce^{3+} =$ 18665 cm^{-1} [12], we can obtain a value of 55735 cm^{-1} (179 nm) as the energy position of the lowest $4f \rightarrow 5d$ transition on Sm^{3+} ion in $YAl_3B_4O_{12}$. This estimation is in agreement with the presence of the features at 174 and 177 nm in the excitation spectra of the Sm^{3+} emission in $YAl_3B_4O_{12}$. Transitions to the higher crystal field components of the Sm^{3+} $4f^45d$ configuration in $YAl_3B_4O_{12}$ are expected at shorter wavelengths and are not observed in the spectra, due to the strong host lattice absorption in this wavelength region. It should be noted that in the 6–8 eV range excitation bands of different nature show a considerable overlap, making the spectra quite difficult to analyze. In this connection, it is interesting to compare the spectra with the results of the electronic structure calculations on $YAl_3B_4O_{12}$. In recent years, the electronic and band structure of $YAl_3B_4O_{12}$ has been studied by using several theoretical approaches. For example, the electronic structure and linear optical properties of $YAl_3B_4O_{12}$ were calculated by Wang et al. [23] using density functional method with the local-density approximation. The authors came to the conclusion that $YAl_3B_4O_{12}$ has an indirect band gap of 6.54 eV and a direct gap of 6.91 eV. The obtained total and partial densities of states (PDOS) indicate that the top valence band is composed of O 2*p*, B 2*s*, and B 2*p* states and the low conduction band mostly consists of Y 4*d* and B 2*p* states. From the calculated absorption spectrum the fundamental absorption edge of $YAl_3B_4O_{12}$ was found to be at 5.4 eV. More recently, Reshak et al. [24] have performed first principles calculations of the band structure and PDOS for $YAl_3B_4O_{12}$ by means of the full-potential linear augmented plane wave method. These authors revealed that the top of the valence band arises from O 2*p* states, whereas states near the bottom of the conduction band have significant contributions from B 2*p*, Y 4*d* and Al 3*s*, 3*p* states. It was shown that $YAl_3B_4O_{12}$ has a direct band gap of 5.1 eV and this value was found to be in reasonable agreement with an experimental one of 5.70 eV [24]. By contrast, in the present work based on the spectra presented in Figs. 1, 2, the optical absorption edge of $YAl_3B_4O_{12}$ was determined at higher energies, viz. at 7.3 eV. Note also that this value is comparable with those (7.1–7.2 eV) reported for other borates whose optical absorption edge is caused by O $2p \rightarrow$ B 2*p*, 2*s* transitions within the isolated BO_3^{3-} groups [25, 26].

The electronic structure of $YAl_3B_4O_{12}$ was also studied using the discrete variational X_α method [5]. The crystal was modeled by a relatively small cluster, consisting of the yttrium ion surrounded by eight BO_3 and six AlO_6 groups. Sketch of the band structure of the $[YAl_6B_8O_{42}]^{39-}$ cluster

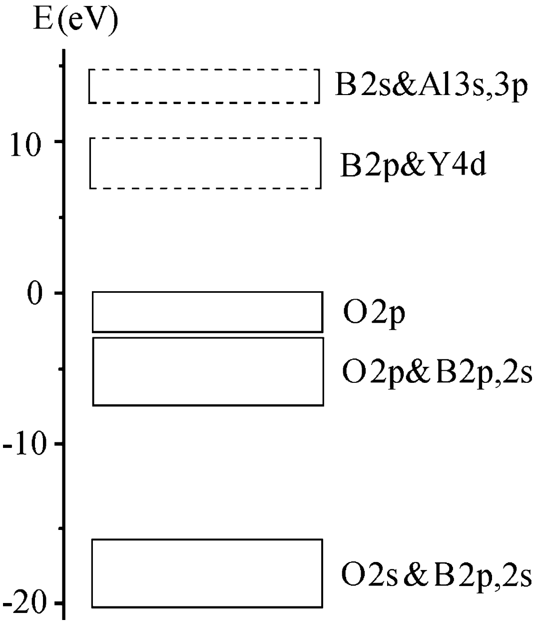

Fig. 3 Sketch of the band structure of $YAl_3B_4O_{12}$

is shown in Fig. 3. It is seen that the valence-band electronic structure is mainly determined by the anionic BO_3^{3-} groups. The highest occupied molecular orbitals have predominantly O 2*p*-character. The molecular orbitals O 2*p*&B 2*p*, B 2*s* are at 2.5–8 eV below the top of the valence band. The O 2*s* orbitals give rise to a relatively broad subband at 16–20 eV below the top of the valence band. The lowest unoccupied molecular orbitals are mainly composed of the B 2*p* orbitals, although some contributions from the Y 4*d* orbitals and, to lesser extent, from Al 3*s*, 3*p* orbitals also take place. The energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital of the cluster under study was found to be 7.32 eV. Despite the relatively small number of atoms involved in the calculations, the qualitative picture of chemical bonding and the calculated electronic structure of $YAl_3B_4O_{12}$ reported by Yoshida et al. [5] seems to be essentially correct.

Conclusions

The luminescence properties of Sm^{3+} ions in $YAl_3B_4O_{12}$ were studied under optical and synchrotron excitation. It was shown that in addition to the $4f \rightarrow 4f$ excitation bands, the excitation spectra of the Sm^{3+} emission contain broad bands at 6.1 and ~7.0 eV. These bands were assigned to and O 2*p* → Sm 4*f* and Sm 4*f* → 5*d* transitions, respectively. Based on the results of electronic structure calculations on $YAl_3B_4O_{12}$, it was found that its optical absorption edge ($E_{edge} = 7.3$ eV) is caused by O 2*p* → B 2*p* transitions within the isolated BO_3^{3-} groups.

References

1. Brenier A (2000) J Lumin 91:121
2. Dekker P, Dawes J (2004) Opt Express 12:5922
3. Dekker P, Dawes J, Piper A (2005) J Opt Soc Am B 22:378
4. Hong HY-P, Dwight K (1974) Mater Res Bull 9:1661
5. Yoshida H, Yoshimatsu R, Watanabe S, Ogasawara K (2006) Jpn J Appl Phys 45:146
6. Kellendonk F, Blasse G (1981) Phys Stat Solidi B 108:541
7. Koporulina EV, Leonyuk NI, Hansen D, Bray KL (1998) J Cryst Growth 191:767
8. Cavalli E, Speghini A, Bettinelli M, Ramirez MO, Romero JJ, Bausa LE, Sole JG (2003) J Lumin 102–13:216
9. Dotsenko VP, Efryushina NP (1992) Phys Stat Solidi A 130:199
10. Dominiak-Dzik G, Solarz P, Ryba-Romanowski W, Beregi E, Kovacs L (2003) J Alloys Comp 359:51
11. Zimmerer G (2007) Radiat Meas 42:859
12. Aloui-Lebbou O, Goutaudier C, Kubota S, Dujardin C, Cohen-Adad MTh, Pedrini C, Florian P, Massiot D (2001) Opt Mater 16:77
13. Yokosawa N, Sato G, Nakazawa E (2003) J Electrochem Soc 150:H197
14. Ogorodnikov IN, Pustovarov VA, Kruzhalov AV, Isaenko LI, Kirm M, Zimmerer G (2000) In: Proceeding of the fifth international conference on inorganic scintillators and their applications SCINT99. Russia, Moscow, p 242
15. Hongpeng Y, Hong G, Zeng X, Kim C-H, Pyun C-H, Yu B-Y, Bae H-S (2000) J Phys Chem Solids 61:1985
16. Dominiak-Dzik G, Ryba-Romanowski W, Kovacs L, Beregi E (2004) Radiat Meas 38:557
17. Blasse G, Bril A (1966) Phys Lett 23:440
18. Dorenbos P (2003) J Phys Condens Matter 15:8417
19. Dorenbos P (2000) J Lumin 91:91
20. Van Pieterson I, Reid MF, Wegh RT, Soverna S, Meijerink A (2002) Phys Rev B 65:045113
21. Bettinelli M, Moncorge R (2001) J Lumin 92:287
22. Reisfeld R, Jorgensen CK (1977) Lasers and excited states of rare earths. Berlin, Springer-Verlag
23. Wang Y, Wang L, Li H (2007) J Appl Phys 102:013711
24. Reshak AliH, Auluck S, Majchrowski A, Kityk IV (2008) Solid State Sci 10:1445
25. Dotsenko VP, Berezovskaya IV, Efryushina NP, Voloshinovskii AS (2002) Mater Chem Phys 77:141
26. Dotsenko VP, Berezovskaya IV, Efryushina NP, Voloshinovskii AS, Stryganyuk GB (2009) Opt Mater 31:1428