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Luminescence and vacuum ultraviolet excitation spectroscopy of samarium doped SrB_4O_7

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ABSTRACT

Sm^{2+} and Sm^{3+} co-doped SrB_4O_7 could be utilized in several high-level optical devices and fundamental knowledge about the optical behavior of these materials benefits the development of luminescent applications. Herein, we report luminescence and its vacuum ultraviolet (VUV) excitation spectra in samarium doped SrB_4O_7 . Both, Sm^{2+} and Sm^{3+} luminescence centers have been examined and distinguished in the emission and the excitation spectra investigated under synchrotron radiation. The contribution of either Sm^{2+} or Sm^{3+} emission lines into the emission spectra heavily depended on the excitation energy, and strong f - f transitions of both Sm^{2+} and Sm^{3+} were detected. At 10 K, a broad intrinsic luminescence in the UV range was detected and attributed to the radiative transition of either bound or self-trapped exciton in SrB_4O_7 . The optical behavior, including e.g. inter-configurational f - d transitions of $\text{Sm}^{(n+)}$ were elucidated with first-principles calculations. Partial density of states well represents the changes of the electronic states that are related to the samarium doping, which in turn explains the emerging features in excitation spectra. In summary, the obtained results clarify the excitation and emission behavior of samarium doped SrB_4O_7 .

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1. Introduction

The strategy how rare-earth (RE) ions are doped in wide band gap materials plays an important role in high-level optical devices and luminescent applications. RE doped materials that emit bright characteristic $4f^n-4f^n$ luminescence are excellent materials to be utilized not only in various practical applications (scintillators, LEDs, color displays *etc.*) but also for medical and scientific purposes, such as in biomedical imaging, and laser technology [1-7]. RE ions can exist in divalent $(RE)^{2+}$ or trivalent $(RE)^{3+}$ states in solids. Depending on the state, the electronic configuration can be given by $4f^n5s^25p^6$ or $4f^{n-1}5s^25p^6$, respectively. Optical properties of RE-doped materials strongly rely on the electronic state of the dopants. Recently, divalent samarium (Sm^{2+}) has been considered as a promising dopant for white-LED applications and for spectral hole burning [8]. Interestingly, trivalent samarium (Sm^{3+}) can constitute an emission component with high quantum efficiency arising from the emitting $^4G_{5/2} 4f^5$ level [4, 9-20]. Overall, combining $Sm^{(n+)}$ activators in wide band gap materials can benefit the optical utilizations [21-24].

Borate has been employed as hosting material in optical devices due to its wide band gap properties [25, 26]. Strontium tetraborate (SrB_4O_7) provides excellent properties, such as high mechanical strength and high optical damage threshold [27]. SrB_4O_7 doped with Sm^{2+} has already been used as an optical pressure sensor [28, 29] and optical thermometer [30]. Sm^{2+} and Sm^{3+} co-doped $BaFCl$ has been employed in X-ray storage phosphors [31] and persistent phosphors [32]. In addition, Sm^{2+} and Sm^{3+} co-doped $NaMgF_3$ has been proposed as a promising dosimeter material [33, 34]. Bright $4f-4f$ transitions of Sm^{2+} and Sm^{3+} , co-doped in SrB_4O_7 , have been reported in UV-IR spectral range [9]. However, $(RE)^{2+}$ and $(RE)^{3+}$ ions also exhibit inter-configurational $4f^n - 4f^{n-1}5d^1$ transitions at high-energy vacuum ultraviolet (VUV) spectral range [4, 35]. These transitions are far less understood. Thus, systematic experimental and theoretical investigation of Sm^{2+} and Sm^{3+} co-doped SrB_4O_7 is needed to understand the electronic structure of these materials and to benefit future design of optical materials.

In addition, stabilities of the Sm^{2+} and Sm^{3+} ions are in question in the doped systems. SrB_4O_7 crystallizes in orthorhombic crystal structure with the space group $Pmn2_1$ (number 31). The structure consists of borate framework that requires oxygen environment for Sm^{2+} stabilization [9]. Dorenbos *et al.* [36] have demonstrated that the stability of a divalent state is related to the energy difference between the $4f^n$ ground state of the lanthanide and the Fermi energy of the matrix compound. In the borate $[BO_4]$ network, boron atoms are tetrahedrally coordinated and each tetrahedron forms a three-dimensional network by corner sharing. The

anhydrous borate with only tetrahedrally coordinated boron atoms is exceptional. Structures that are more general are accompanied with an oxygen ion, coordinated by three boron atoms. All boron and oxygen atoms in the $[\text{BO}_4]$ network are involved building channels parallel to the b and c lattice directions, and strontium ions fit into these channels. The substitution of samarium leads to formation of both center types, Sm^{2+} and Sm^{3+} [9].

Herein, we report a systematical investigation of Sm^{2+} and Sm^{3+} co-doped SrB_4O_7 . Synchrotron radiation-induced luminescence and vacuum ultraviolet (VUV) excitation spectra were recorded to study charge migrations during the de-excitation and excitation processes within the doped systems. Origins of the spectral features were further investigated by first-principle calculations, performed in the cases of pure SrB_4O_7 and the borate system doped with both Sm^{2+} and Sm^{3+} centers. Besides fundamental understanding of the optical properties of these materials, we believe that atomic-level exploration of this RE-doped borate will facilitate design and development of high-performance luminescent materials in future optical applications.

2. Materials and methods

Samarium doped strontium tetraborate (SrB_4O_7) samples were synthesized using a traditional solid-state method, based on the interaction of boron oxide and strontium (samarium) oxide at high temperature. Initial materials were Sm_2O_3 (99.9% Alfa-Aesar), SrCO_3 (99.9% Sigma-Aldrich) and H_3BO_3 (99.5% Merck). The 5wt% excess of boric acid was added due to preferential evaporation of boron oxide. Series of $\text{Sr}_{1-x}\text{Sm}_x\text{B}_4\text{O}_7$ samples with $x=0.005, 0.010, 0.025, 0.050$ and 0.100 were prepared, corresponding to 0.5%, 1.0%, 2.5%, 5.0% and 10.0% of samarium substitution. The details of this particular synthesis have been reported in [9]. In order to get samples in homogeneous crystal phase, a three step annealing procedure at 900°C was applied for 8h in air with subsequent X-ray diffraction (XRD) analysis (see details in [9]). Pure orthorhombic phase for SrB_4O_7 (ICDD#04-006-8398) was achieved in samples with samarium concentration below 5.0%. The sample with 10% samarium concentration revealed a small fraction of additional monoclinic SmB_3O_6 phase (ICDD#04-010-0838) [9].

Synchrotron radiation has been successfully applied for luminescence studies of many types of wide band gap inorganic materials in UV and VUV spectral ranges [37-43], including nanocrystalline semiconductor structures [44, 45] and two-dimensional systems [46-48]. Luminescence properties of samarium doped SrB_4O_7 were studied experimentally using the DORIS III storage ring of DESY (Hamburg, Germany). The excitation (3.7–25 eV) and the

emission (200-800 nm) spectra were measured in 10-300 K temperature range at the Superlumi endstation of I3 beamline [49].

Geometric optimization and electronic structure analysis were carried out by employing density functional theory (DFT) code with the Cambridge Serial Total Energy Package (CASTEP) software [50]. The exchange-correlation functional was approximated with the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) functional [51]. The convergence tolerance of the energy was set to 10^{-6} eV. A cut-off energy of 570 eV was employed to expand the plane waves included in the basis set. As it is well-known that GGA underestimates the band gap of *f*-electron systems, GGA+*U* approximation was employed with $U = 6.0$ eV. The Brillouin Zone integrations were carried out on a $2 \times 2 \times 1$ Monkhorst–Pack k-points grid for geometry optimization, and a $4 \times 4 \times 1$ k-points grid for band structure and density of states (DOS) calculations.

In the first-principle optimization, we used the experimental lattice constants and atomic positions [52-54] of SrB_4O_7 to initialize relaxation. Optimized structures for both pure and Sm^{n+} doped SrB_4O_7 are depicted in Fig. 1a-c. The optimized lattice parameters, $a=10.996\text{\AA}$, $b=4.5419\text{\AA}$, and $c=4.356\text{\AA}$ were in reasonable agreement with previous results [52-55]. Since it is computationally demanding to go for larger supercells, the $3 \times 2 \times 2$ cells of $\text{Sr}_{24}\text{B}_{96}\text{O}_{168}$ host was considered in this work. Sm^{2+} was substituted to the site of Sr^{2+} to simulate a Sm^{2+} doped system. Sm^{3+} cannot substitute B^{3+} site because of the large difference in ionic radii of these ions. Therefore, substitution of Sr^{2+} by Sm^{3+} is only possible by introducing Sm^{3+} to the SrB_4O_7 lattice. In this case, however, a charge compensator is needed. The excess positive charge can be compensated with impurities or lattice defects. As we did not detect any other impurities in our samples except samarium, we used a simple charge compensator – one Sr^{2+} vacancy for two Sm^{3+} ions. In other words, charge compensation was taken care of by introducing a vacancy such as $3\text{Sr}^{2+} \rightarrow 2\text{Sm}^{3+}$ and a vacancy at the Sr^{2+} site (Fig.1c). Finally, the crystal structure was re-optimized after substitution with Sm^{2+} and Sm^{3+} ions.

[Fig. 1. near here, figures can be found after the reference list]

3. Results and discussion

Emission spectra of the sample with 1% samarium concentration under different excitation energies are shown in Fig. 2. Obviously, these emission spectra strongly depend on the

excitation energy. Each spectrum contains several emission lines, which presumably belong to radiative transitions in samarium ions. For instance, the intensive well-known $4f^5-4f^6$ transitions of Sm^{3+} ($^4\text{G}_{5/2} - ^6\text{H}_{(5,7,9)/2}$) are clearly seen under $\lambda_{\text{exc.}}=150$ nm excitation. These visible transitions have been reported earlier for samarium doped strontium tetraborates by Sakirzanovas *et al.* [9], as well as in some other Sm^{3+} doped complex oxides [56-59]. On the other hand, under $\lambda_{\text{exc.}} = 300$ nm, it is possible to observe the main intensive transitions ($^5\text{D}_0 - ^7\text{F}_{n(=0,1,\dots,4)}$) of Sm^{2+} within the $4f^6$ configuration. Under 300 nm excitation, Sm^{3+} transitions are only weakly observed. The observed Sm^{2+} transitions have been reported previously for many compounds, including SrB_4O_7 [9, 60-62]. The synthesis and presence of samarium divalent impurities in SrB_4O_7 have met some practical problems before, as described in more detail in [63]. However, the luminescence spectra reveal the presence of Sm^{2+} ions in the measured samples.

When the excitation energy exceeds the band gap energy of SrB_4O_7 ($\lambda_{\text{exc.}}=90$ nm in Fig. 2), the spectrum contains emission lines native to both Sm^{2+} and Sm^{3+} . It is worthwhile to note that the emission spectra do not depend on samarium concentration. To elaborate, the same emission lines can be observed for all the studied samples with different samarium concentration using same excitation energies (Figures S1, S2 and S3 in the Supplementary material).

[Fig. 2. near here]

In addition to the Sm^{2+} and Sm^{3+} emissions, we observed a broad emission band peaking at 300 nm in the samples with a low samarium concentration at low temperature. Fig. 3 shows the emission spectrum of the 0.5% samarium-doped sample at 10 K under high-energy excitation (90 nm or 13.78 eV). The high-resolution emission spectra of Sm^{2+} and Sm^{3+} under different excitations are shown in Fig. S4. The contribution of either Sm^{2+} or Sm^{3+} lines into total emission spectra depends on the excitation energy similarly to the spectra observed at room temperature (Fig. 2). The intensity of the 300 nm emission is much weaker than the samarium lines. This band is most likely caused by a radiative recombination of a self-trapped exciton (STE). To our knowledge, such intrinsic STE emission in SrB_4O_7 has not been reported before.

[Fig. 3. near here]

The emission spectra in Fig. 2 clearly show that the contribution of each emission (Sm^{2+} or Sm^{3+}) to the total emission spectrum depends on the excitation energy. For deeper

understanding, UV-VUV excitation spectra were measured. The excitation spectra of Sm^{2+} emission ($\lambda_{\text{em}} = 684 \text{ nm}$) and Sm^{3+} emission ($\lambda_{\text{em}} = 590 \text{ nm}$) are depicted in Fig. 4 and 5 for all the samples. Each excitation spectrum of Sm^{2+} ($^5\text{D}_0 - ^7\text{F}_0$ transition at 684 nm) exhibits more than one excitation band below 5 eV. These excitations are attributed to the first inter-configurational $4f^6 - 4f^5 5d^1$ ($f-d$) transitions of Sm^{2+} . Similar excitations have been observed before by Sakirzanovas et al. [9], who have explained these transitions by splitted $5d$ levels of Sm^{2+} in SrB_4O_7 , coupled with $4f^5(^6\text{H}_j)$ and $4f^5(^6\text{F}_j)$ core electron substates. There are also other excitation bands in the 5-7 eV excitation range, located at a bit higher energies than the first inter-configurational $f-d$ transitions of Sm^{2+} . We hypothesize that these excitation bands could be caused by higher-energy $f-d$ transitions.

[Fig. 4 near here]

The excitation peak at 9.7 eV (127 nm) in Fig. 4 is likely to have excitonic origin i.e. it can be due to energy transfer from a self-trapped (STE) or bound exciton (BE) to the Sm^{2+} center. The intensity of this excitonic band is relatively small in respect of the band-to-band excitation in SrB_4O_7 , which is higher than 10 eV (see discussion about the band gap energy below). The excitation curve at energy higher than 10 eV is represented as an intensive monotonous growth from the band gap energy (E_g) up to the 20-25 eV (i.e. $E \approx 2E_g$) excitation range. Mikhailin [64 and references therein] has summarized data of high-energy excitation spectra for many inorganic compounds excited by VUV photons. In according to Mikhailin's analysis, the monotonous growth of the excitation intensity from E_g value to $2E_g$ refers to a generation of electron-hole pairs in Sm^{2+} doped SrB_4O_7 and is associated to the relaxation processes and energy transfer mechanisms of the system. Thus, the excitation spectra (Fig. 4) indicate that the recombination mechanism of energy transfer from the host lattice to Sm^{2+} ions occurs in SrB_4O_7 .

The excitation spectra of Sm^{3+} emission, measured in $^4\text{G}_{5/2} - ^6\text{H}_{7/2}$ emission line at 590 nm, show various bands between the 5 – 10 eV spectral range (Fig. 5). These bands are located at higher energies than the excitations observed from Sm^{2+} doped SrB_4O_7 . This is the reason why only the Sm^{2+} emission lines can be observed under low energy excitations (Fig. 2 bottom). It can be assumed that the excitation bands around 5–7 eV are caused by the first (lowest-energy) inter-configurational $4f^5 - 4f^4 5d^1$ transitions. Similar results have been reported by Ryba-Romanowski et al., who have estimated that the first $f-d$ transition of Sm^{3+} are located at 6.25 - 6.81 eV in LSO, GSO, and LGSO single crystals [10]. Additionally, the excitation spectrum of Sm^{3+} emission shows various peaks between 7-10 eV. These bands can

be attributed to the f - d transitions *e.g.* from lower f -states to higher $5d$ crystal components of Sm^{3+} . Solarz et al. have detected similar peaks in Sm^{3+} doped $\text{KZnLa}(\text{PO}_4)_2$ [65]. On the other hand, the excitation peaks around 7-9 eV could be caused by a charge-transfer process from $\text{Sm}^{3+} 4f^5$ shell to the conduction band of SrB_4O_7 . This type of behavior in the same spectral range has been reported by Nakazawa et al. for Sm^{3+} doped in variety of host matrixes, however not in SrB_4O_7 [35]. Furthermore, the excitation peaks in 7-10 eV spectral range can partially belong to the transitions due to ionization of $5d$ states of Sm^{3+} as discussed in more detail in [66]. Such transitions are located at slightly higher energies than $4f$ - $5d$ transitions but below those of excitonic transitions. Usually, $4f$ - $5d$ transitions overlap with the $5d$ ionization transition and can be separated by means of time-resolved spectroscopy experiments under VUV excitations. As an example, an extraction of $5d$ ionization transitions in Ce^{3+} doped $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ has been studied before in [67]. However, the same experiments could not be performed in this research, since the decay time of Sm^{3+} is much longer than the time window between excitation bunches of DORIS III storage ring had. The excitation spectra of Sm^{3+} emission at energies higher than band gap transitions are similar to the excitation spectra for Sm^{2+} emission. This means that the recombination mechanism of the energy transfer occurs from host lattice to the samarium ions independently on different samarium charge states.

[Fig. 5. near here]

Excitation spectra of the 300 nm emission in Fig. 3 (STE) are presented in Fig. 6. This spectrum has a distinct intensive excitonic peak at about 10 eV with subsequent decrease of the intensity. Further growth of the excitation curve occurs at energies higher than 20 eV (*i.e.* at $E \approx 2E_g$), where multiplications of electronic excitations occur through carrier multiplication process. Such behavior is typical for excitons [37, 41, 64, 68, 69] under high-energy excitation, through a process called multiple exciton generation. This indirectly confirms our suggestion about the excitonic origin of the 300 nm emission band (Fig. 3). It can be clearly seen that the excitation spectrum for the STE emission differs from the corresponding spectra of Sm^{2+} and Sm^{3+} emissions in Fig. 6, where the recombination mechanism of the energy transfer was indicated. The excitation spectra of Sm^{2+} and Sm^{3+} emissions, obtained at low temperature (Fig. 6), are similar to the corresponding spectra measured at room temperature (Fig. 4 and 5). However, the inter-configurational f - d transition peaks of the Sm^{2+} excitation spectra are better resolved at low temperature. The excitation spectra of Sm^{2+} emissions (both for room and low temperatures) also reveal the weak excitonic peak right below 10 eV. We assume that this peak results from re-absorption of the

excitonic emission by Sm^{2+} , since the STE emission overlaps well with the excitation of f - d transitions (below 5 eV) in Sm^{2+} (the f - d excitation lines in the dotted area in Fig. 6). Sm^{3+} does not have excitation bands in this spectral range and, therefore, the excitonic peak is absent in any excitation spectra of Sm^{3+} .

[Fig. 6. near here]

To illustrate the experimental results in more detail, the partial density of states (PDOS) of pristine SrB_4O_7 crystal and the Sm^{2+} and Sm^{3+} doped SrB_4O_7 are shown in Fig. 7a-c. For pure SrB_4O_7 , indirect and direct band gap values calculated with DFT are 9.56 eV and 10.32 eV as can be seen from the calculated band structure in Fig. 8. The values are lower than the experimental results due to underestimation from GGA+U, but in agreement with previous theoretical studies [55]. As can be seen from the Fig. 7b-c, the doping of Sm^{2+} and Sm^{3+} atoms in SrB_4O_7 has a clear effect on the results of the PDOS calculations. The doped samarium cations contribute to additional $4f$ orbital defect states to the band gap of SrB_4O_7 , which are naturally not obtained in the pristine SrB_4O_7 in Fig. 7a. The energy levels caused by the substitution clearly depend on the charge state of samarium.

[Fig. 7. near here]

Although standard DFT is known to underestimate the band gap of systems with strongly correlated electrons, our calculations based on the versatile GGA method renders a qualitative comparison with the obtained experimental results. The PDOS calculations in Fig. 7a-c support most of our analysis related to the experimental excitation spectra. As discussed above, the excitation bands of Sm^{2+} below 5 eV in Fig. 4 can be attributed to the inter-configurational transitions from f - to d -orbital. Nevertheless, the trend of the shift of the band gaps obtained in the PDOS calculations provides explanation for the associated experimental phenomena in SrB_4O_7 [55]. From the qualitative perspective, the PDOS of $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$ has broader d -states, lying at 3.9 eV as can be seen from Fig. 7b. Hence, the f -orbital state at -0.1 eV can be excited to this wide d -orbital, probably leading to the origin of excitation band peaks below 5 eV in the experimental spectra. The higher-energy excitation bands in the 5-7 eV excitation range, reflected in the excitation spectrum of Fig. 4 may originate from the transitions of Sm^{2+} f -state at -0.7 eV to d -state at 3.9 eV.

The PDOS calculations in Fig. 7 are also in a good agreement with the Sm^{3+} excitation spectra. The first experimental excitation peak at around 5.6 eV in Fig. 5 may correspond to the excitation from the f -orbital state at around -0.2 eV to broader $5d$ -orbital contribution

around 4.9 eV that can be seen from Fig. 7c. The next peak at around 6.3eV in experiment could result from the transition from the same *f*-orbital contribution at -0.2 eV to the next *d*-orbital contribution around 5.3 eV. The higher-energy excitations, observed experimentally in the 7-9 eV spectral range could correspond to the transitions from the lower *f*-states that are located in the valence band (between -2 eV and -1 eV) to the *d* states around 4.9-6eV. Related to these higher-energy transitions, the PDOS calculations in Fig. 7 a-c suggest that there are new energy levels appearing in the valence band, introduced by the $\text{Sm}^{(n+)}$ ions, which enable different *f-f* and inter-configurational *f-d* transitions to occur.

[Fig. 8. near here]

The position of the excitonic excitation peak of STE emission corresponds to the band gap energy of SrB_4O_7 being higher than 10 eV. This result is very close to the previous calculations of Wang et al., who have obtained the SrB_4O_7 direct band gap as 11.18 eV [55]. They also previously determined the value of the indirect band gap as 9.71 eV [55]. Throughout this study, we obtained an indirect and direct band gap of 9.56 eV and 10.32 eV, respectively for pristine SrB_4O_7 (Fig. 8). It should be noted that a ‘scissors operator’ with energy of 2.4 eV was selected for the band gap of SrB_4O_7 following prior work [55] since DFT calculations typically underestimate the band gap values of strongly correlated systems. Due to the same reason, the energy differences between the $\text{Sm}^{(n+)}$ electronic states in the band gap are also slightly underestimated as can be seen from the comparison with the experimental spectra. However, the transitions between the calculated states are relatively close to the experimental values. The concentration of Sm^{2+} and Sm^{3+} is about 1% in all of our calculations. A small change of the doping concentration (*e.g.* from 0.5% to 1%) would lead to a subtle impact on electronic structure of the dilute $\text{Sm}^{(n+)}$ -doped SrB_4O_7 systems. Overall, the present PDOS results are qualitatively valid to explain the experimental findings.

4. Conclusions

In the present work, luminescence and VUV excitation properties of Sm^{2+} and Sm^{3+} doped SrB_4O_7 were studied by luminescence and VUV spectroscopy, using synchrotron radiation. The experimental results have been compared to the partial density of states (PDOS) calculations conducted for pure, as well as Sm^{2+} - and Sm^{3+} -doped SrB_4O_7 . Results of the luminescence emission measurements show that depending on the excitation energy, the observed emission is related to either Sm^{2+} or Sm^{3+} . Additionally, intrinsic emission was detected in SrB_4O_7 and attributed to the self-trapped exciton (STE). To our best knowledge,

this type of behavior in SrB_4O_7 has not been reported before. The analysis about the STE emission was indirectly confirmed through excitation measurements and an intensive STE excitation band was detected at around 10 eV, which is close to the calculated band gap value of SrB_4O_7 . Furthermore, charge multiplication processes were detected at energies higher than 20 eV (about $2E_g$) by further growth of the excitation curve. Additionally, the experimental excitation spectra showed inter-configurational Sm^{2+} and Sm^{3+} *f-d*-transitions and our calculations support the experimental observations. In summary, this study clarified excitation and emission behavior of samarium doped SrB_4O_7 with coherent results between our experimental results and first-principles calculations.

Supplementary materials

See supplementary material for experimental emission spectra with different samarium concentrations under 90 nm, 150 nm, and 300 nm excitations at room and low (10 K) temperature.

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Figure captions

- Fig. 1. The optimized crystal structure of SrB_4O_7 : (a) the unit cell (b) the $3 \times 2 \times 2$ supercell of SrB_4O_7 , doped with Sm^{2+} and (c) Sm^{3+} cations. The red, pink, green and blue spheres represent the O, B, Sr and Sm atoms, respectively. The dash-dot ball refers to $3\text{Sr}^{2+} \rightarrow 2\text{Sm}^{3+}$ and a vacancy at Sr^{2+} site.
- Fig. 2. The luminescence spectra of $\text{SrB}_4\text{O}_7:\text{Sm}$ (1%) under different excitation energies at room temperature. The line at 600 nm in the emission spectra under 300 nm excitation (bottom graph) is due to the second order of excitation wavelength.
- Fig. 3. The luminescence spectra of intrinsic and samarium related emissions in $\text{SrB}_4\text{O}_7:\text{Sm}$ (0.5%) under 90 nm (13.78 eV) excitation at 10 K
- Fig. 4. The excitation spectra of Sm^{2+} emission ($^5\text{D}_0$ - $^7\text{F}_0$ at 684 nm) in $\text{SrB}_4\text{O}_7:\text{Sm}$, having different samarium concentrations at room temperature. The spectra are normalized at 300 nm. Arrows show the excitation energies of the emission spectra in Fig. 2.
- Fig. 5. The excitation spectra of Sm^{3+} emission ($^4\text{G}_{5/2}$ - $^6\text{H}_{7/2}$ at 590 nm) in $\text{SrB}_4\text{O}_7:\text{Sm}$, having different samarium concentrations at room temperature. The spectra are normalized at 150 nm. The arrows show the excitation energies of the emission spectra in Fig. 2.
- Fig. 6. The excitation spectra of Sm^{2+} ($^5\text{D}_0$ - $^7\text{F}_0$ at 684 nm, red), Sm^{3+} ($^4\text{G}_{5/2}$ - $^6\text{H}_{7/2}$ at 590 nm, blue) and intrinsic (300 nm, black) emissions in $\text{SrB}_4\text{O}_7:\text{Sm}$ (0.5%) at 10 K
- Fig. 7. The electronic PDOS for (a) pure SrB_4O_7 with 2.4 eV scissor operator (b) SrB_4O_7 doped with Sm^{2+} and (c) SrB_4O_7 doped with Sm^{3+} cation. The PDOS is obtained by Gaussian extension applied to the eigenvalues. The broadening width parameter is chosen to be 0.1 eV and the vertical dash-dot lines indicate the Fermi level.
- Fig. 8. Calculated band structure of SrB_4O_7 . The energies of the bands are plotted with respect to the Fermi level.

(a) a primitive unit cell

(b) $\text{SrB}_4\text{O}_7\text{Sm}^{2+}$

(c) $\text{SrB}_4\text{O}_7\text{:Sm}^{3+}$

Highlights

- Luminescence and VUV excitation spectra of $\text{Sm}^{(n+)}$ ions in SrB_4O_7 are demonstrated
- First principle calculations of Sm^{2+} and Sm^{3+} ions in SrB_4O_7 are performed
- Energy transfer process from SrB_4O_7 host lattice to $\text{Sm}^{(n+)}$ centers are suggested
- Multiplications of electronic excitations region in SrB_4O_7 is identified
- The excitation spectrum of self-trapped exciton emission in SrB_4O_7 is obtained

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: