

Charge transfer luminescence of hafnates under synchrotron vacuum ultraviolet excitation†

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Under synchrotron vacuum ultraviolet excitation, three different hafnates ($\text{BaHf}(\text{PO}_4)_2$, $\text{BaHf}(\text{BO}_3)_2$ and $\text{BaHfSi}_3\text{O}_9$) show self-activated luminescence with peaks ranging from 275–335 nm, which is attributed to the charge-transfer luminescence from the hafnate (HfO_6^{8-}) group. Upon doping Eu^{2+} into $\text{BaHfSi}_3\text{O}_9$, host sensitization of Eu^{2+} emission via hafnate intrinsic emission is demonstrated.

Oxide compounds consisting of transition-metal ions without d-electrons, such as titanates, vanadates, molybdates, niobates and tungstates, are known to luminesce.¹ The mechanism responsible for the observed luminescence is the ligand-to-metal charge transfer (LMCT).¹ The corresponding charge transfer absorptions in these compounds are found to be generally situated in the ultraviolet region.¹ Recent studies on LMCT from transition-metal ions have been extended to zirconates, in which Zr^{4+} with a d^0 configuration plays an important role.^{2,3} Unlike these transition-metal containing compounds mentioned above, the charge transfer (CT) absorptions of zirconates are found to locate at a much higher energy level,^{2,3} and generally it requires the excitation light to have an energy in the vacuum ultraviolet region (VUV; $E > 50\,000\text{ cm}^{-1}$; $\lambda < 200\text{ nm}$) so that zirconates can be excited into their charge transfer state.^{2,3} Hf^{4+} belongs to the same fourth group element as that of Ti^{4+} and Zr^{4+} , thus CT luminescence is expected from hafnates as well. However, after examining the existing literature, only a few works on the luminescence of hafnates were reported, among which most are focused on the X-ray excited luminescence,^{4–7} partially for the purpose of developing phosphor for medical X-

ray imaging applications. Examples are $\text{BaZr}_{1-x}\text{HfPO}_4$,⁴ Li_2HfO_3 ,⁵ HfP_2O_7 ,⁶ $\text{Hf}_{1-x}\text{Zr}_x\text{GeO}_4$.⁷ From these works, we aware that hafnates can give luminescence upon X-ray excitation, but information regarding their absorption is still rare. The lack of studies for the charge transfer luminescence from hafnates is presumably due to the technique and method of conventional UV excitations that are unable to excite hafnates, as is the case for zirconates. With the advancement of synchrotron radiation, it is possible to investigate the photoluminescence properties of phosphors in VUV region. Investigation of spectroscopic properties of a material in the VUV region provides important and instructive information needed for engineering VUV phosphors used for PDPs and Hg-free lamp. In this paper, we investigated the CT luminescence of three different hafnates ($\text{BaHf}(\text{PO}_4)_2$, $\text{BaHf}(\text{BO}_3)_2$ and $\text{BaHfSi}_3\text{O}_9$) which have HfO_6^{8-} group in their crystal structure using synchrotron VUV excitation. In addition, Eu^{2+} has been widely used as the luminescent center for phosphor applied in lighting and displays,⁸ with an aim to develop new VUV phosphor, we also studied the VUV-excited luminescence of Eu^{2+} -doped $\text{BaHfSi}_3\text{O}_9$ and demonstrated the unprecedented host sensitization of Eu^{2+} emission using hafnate intrinsic emission.

Samples of undoped $\text{BaHf}(\text{PO}_4)_2$, $\text{BaHf}(\text{BO}_3)_2$, $\text{BaHfSi}_3\text{O}_9$ and Eu^{2+} -doped $\text{BaHfSi}_3\text{O}_9$ were prepared in powder form by using high temperature solid state reaction methods. The phase purity of all samples was checked by using powder X-ray diffraction (XRD) analysis. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured at BL03A beamline of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. Samples synthesis details and experimental setup for photoluminescence spectra are provided as Supplementary Information.

Fig. 1 shows the XRD patterns of $\text{BaHf}(\text{BO}_3)_2$, $\text{BaHf}(\text{PO}_4)_2$ and $\text{BaHfSi}_3\text{O}_9$ synthesized in present work. Since no reported standard XRD pattern is available for $\text{BaHf}(\text{BO}_3)_2$ and $\text{BaHfSi}_3\text{O}_9$, their phase purity was identified by using the XRD data of the corresponding zirconate as a reference. The XRD patterns of

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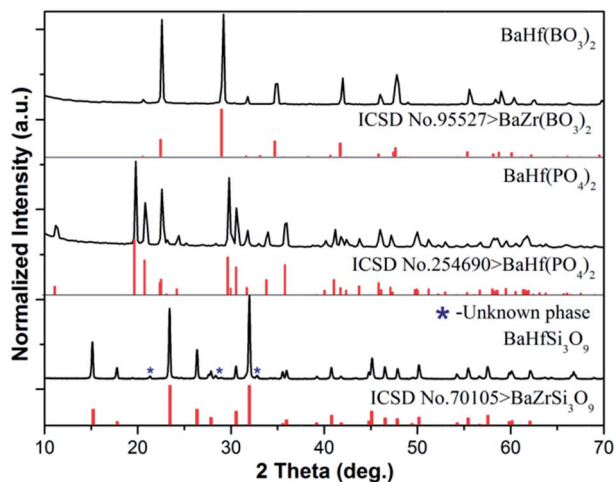


Fig. 1 XRD patterns of $\text{BaHf}(\text{BO}_3)_2$, $\text{BaHf}(\text{PO}_4)_2$ and $\text{BaHfSi}_3\text{O}_9$.

the three hafnates are in good agreement with the reference data reported in ICSD no. 254690 for $\text{BaHf}(\text{PO}_4)_2$, ICSD no. 95527 for $\text{BaZr}(\text{BO}_3)_2$ and ICSD no. 70105 for $\text{BaZrSi}_3\text{O}_9$, with the exception of an unknown phase marked by an asterisk ($I\% < 4\%$, $2\theta = 21.1^\circ$, 28.3° and 32.8°) observed in $\text{BaHfSi}_3\text{O}_9$ (Fig. 1). This observation indicates that each hafnate retained the same crystal structure as that of its corresponding zirconate. Previous structural study on $\text{BaHf}(\text{PO}_4)_2$ (ref. 9), $\text{BaZr}(\text{BO}_3)_2$ (ref. 10) and $\text{BaZrSi}_3\text{O}_9$ compounds (ref. 11) has shown that a Zr–O octahedron unit exists in their crystal structures. Due to the similar XRD patterns between the zirconate and hafnate, we suggest the hafnium is six-coordinated in all of the three hafnates under investigation.

Fig. 2 shows the normalized PLE and PL spectra of $\text{BaHf}(\text{BO}_3)_2$, $\text{BaHf}(\text{PO}_4)_2$ and $\text{BaHfSi}_3\text{O}_9$. Under excitation at 172 nm, $\text{BaHf}(\text{PO}_4)_2$, $\text{BaHf}(\text{BO}_3)_2$ and $\text{BaHfSi}_3\text{O}_9$ show broad emission with maxima at 335 nm, 320 nm and 275 nm, respectively. We set the excitation light at 172 nm because in practice the available VUV light source (Xe/Ne excimer

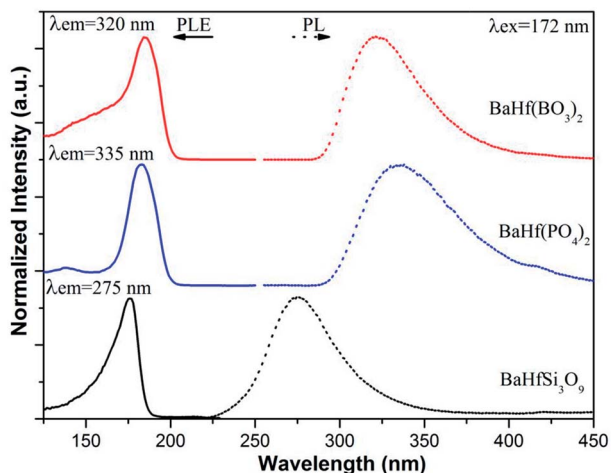


Fig. 2 PL and PLE spectra of $\text{BaHf}(\text{BO}_3)_2$, $\text{BaHf}(\text{PO}_4)_2$ and $\text{BaHfSi}_3\text{O}_9$.

discharge) gives the main emission at this wavelength. This observation suggests that hafnates may serve as UV-emitting phosphors and find their new applications in transcription of repair enzymes and treatment of skin diseases such as psoriasis *et al.*¹² In analogy to the case of the VUV-excited luminescence of zirconates,^{1–3} the observed broad emission is assigned to the CT luminescence from the hafnate (HfO_6^{8-}) group, which can be explained as the recombination of the excited electron on Hf^{4+} ions with hole left on O^{2-} ligand during the CT absorption process. In reality, it is considered that the charge transfer transition doesn't involve in transferring one electron but does involve a considerable reorganization of the charge density distribution around the metal ion.¹³ The PLE spectra for these three hafnates obtained by monitoring the emission maximum of each compound are all composed of an intense band in the range of 125–200 nm with peaks at 185 nm, 184 nm and 176 nm for $\text{BaHf}(\text{PO}_4)_2$, $\text{BaHf}(\text{BO}_3)_2$ and $\text{BaHfSi}_3\text{O}_9$, respectively, which is attributed to the charge transfer transition from ligand O^{2-} to metal Hf^{4+} , *i.e.*, electron is transferred from the 2p orbital of the surrounding O^{2-} ions into the empty 5d orbital of Hf^{4+} . After electron transfer to Hf^{4+} , the hole appears to be distributed over ligands around the Hf^{3+} ion. In the reverse process, the radiative recombination of electron at Hf^{3+} (formed after electron transfer) with the hole localized on O^{2-} gives rise to the observed charge transfer luminescence. According to the Forster–Dexter energy transfer theory,¹⁴ resonant energy transfer from a sensitizer to an acceptor happens when certain conditions are met, *i.e.*, (1) a considerable spectral overlap between the sensitizer's emission and acceptor's absorption, and (2) a reasonable distance between the sensitizer and acceptor.¹⁴ In our previous work, Eu^{2+} has been shown to have a broad 4f–5d absorption ranging from 280–400 nm in $\text{BaHfSi}_3\text{O}_9\text{-Eu}^{2+}$,¹⁵ while in present work the hafnate group in $\text{BaHfSi}_3\text{O}_9$ gives broad UV emission with maximum at 275 nm under VUV excitation (see Fig. 2). This fact provides the beneficial conditions for energy transfer from hafnate group to Eu^{2+} based on the Forster–Dexter energy transfer theory, and implies that the CT emission from hafnates could be utilized to sensitize Eu^{2+} emission in $\text{BaHfSi}_3\text{O}_9\text{-Eu}^{2+}$ upon VUV excitation. To see whether sensitization of Eu^{2+} emission by hafnates CT luminescence occurs, we measured the PL spectra of $\text{BaHfSi}_3\text{O}_9$ doped with various concentrations of Eu^{2+} (see Fig. 3) under 172 nm excitation. When 2% Eu^{2+} is introduced into $\text{BaHfSi}_3\text{O}_9$, it is found that the CT luminescence from hafnate is greatly reduced. With further increasing the Eu^{2+} doping concentration, accompanied by an increase of Eu^{2+} 5d–4f emission at 474 nm, the charge transfer luminescence from hafnate decreases further, demonstrating that energy transfer from hafnate group to Eu^{2+} indeed occurs *via* hafnate CT luminescence. The CT luminescence from hafnate group is almost quenched due to such energy transfer when the Eu^{2+} doping concentration is increased to 6%. With increasing Eu^{2+} doping concentration, more Eu^{2+} ions are distributed in the host matrix, thus the energy transfer probability between hafnate group and Eu^{2+} is increased, resulting in the observation that the CT luminescence decreases while the Eu^{2+} emission increases with increasing Eu^{2+} dopant concentration.

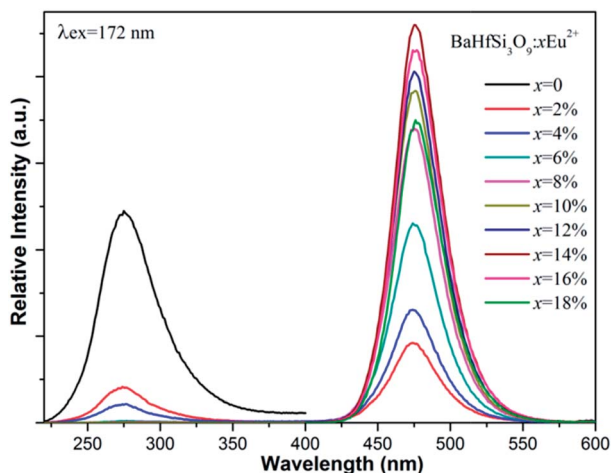


Fig. 3 PL spectra of $\text{BaHfSi}_3\text{O}_9:x\text{Eu}^{2+}$ ($0 \leq x \leq 18\%$) under excitation at 172 nm.

When Eu^{2+} doping concentration is increased to 14%, Eu^{2+} emission starts to decrease due to concentration quenching.

Fig. 4 presents the PL excitation spectra of a 2% Eu^{2+} doped sample detected by monitoring the two emission bands located at 275 nm and 474 nm together with the PL spectrum of host matrix $\text{BaHfSi}_3\text{O}_9$. The PLE spectrum detecting Eu^{2+} emission and that detecting hafnate CT luminescence has a similar absorption band below 200 nm assigned to $\text{Hf}^{4+}-\text{O}^{2-}$ charge transfer absorption. The small shift for the $\text{Hf}^{4+}-\text{O}^{2-}$ charge transfer absorption band observed in the PL excitation spectra probably due to the emission grating blazes differently at 275 nm and 474 nm. The presence of the $\text{Hf}^{4+}-\text{O}^{2-}$ CT absorption band in the excitation spectrum monitored within the Eu^{2+} emission further indicates that the energy transfer from hafnate group to Eu^{2+} ions via $\text{Hf}^{4+}-\text{O}^{2-}$ CT luminescence has occurred. The two additional bands above 200 nm in the PLE spectrum

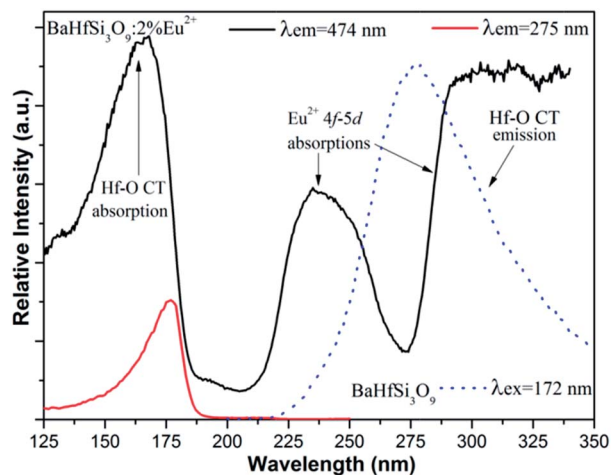


Fig. 4 PLE spectra of $\text{BaHfSi}_3\text{O}_9-2\% \text{Eu}^{2+}$ monitoring Hf–O charge transfer emission at 275 nm (red solid line) and Eu^{2+} 5d–4f emission at 474 nm (black solid line) together with the PL spectrum of host $\text{BaHfSi}_3\text{O}_9$ (blue dot line), respectively.

monitoring the Eu^{2+} emission (that are not observed in the PL spectrum monitoring $\text{Hf}^{4+}-\text{O}^{2-}$ CT luminescence) are assigned to the 4f–5d absorption of Eu^{2+} due to crystal field splitting. The perfect spectral overlap between Hf–O CT emission and Eu^{2+} 4f–5d absorption provides favorable conditions for energy transfer from hafnate group to Eu^{2+} . Process of $\text{Hf}^{4+}-\text{O}^{2-}$ CT luminescence and energy transfer from hafnate intrinsic emission to Eu^{2+} is schematically illustrated in Scheme S1 (ESI[†]).

In summary, photoluminescence of three different hafnium-containing compounds, $\text{BaHf}(\text{PO}_4)_2$, $\text{BaHf}(\text{BO}_3)_2$ and $\text{BaHfSi}_3\text{O}_9$, has been studied using synchrotron vacuum ultraviolet excitation. These three hafnates show absorption in the region of 125–200 nm with a maximum close to 180 nm, which results from charge transfer from O^{2-} ligand to Hf^{4+} metal. Under VUV excitation at 172 nm, $\text{BaHf}(\text{PO}_4)_2$, $\text{BaHf}(\text{BO}_3)_2$ and $\text{BaHfSi}_3\text{O}_9$, show self-activated luminescence peaking at 335 nm, 320 nm and 275 nm, which is attributed to the charge-transfer luminescence from the hafnate (HfO_6^{8-}) group, and can be rationalized as the recombination of the excited electron on Hf^{4+} ions with the hole left on the O^{2-} ligand created during the charge transfer absorption. Upon doping Eu^{2+} into the host matrix of $\text{BaHfSi}_3\text{O}_9$, sensitization of Eu^{2+} emission via $\text{Hf}^{4+}-\text{O}^{2-}$ charge transfer luminescence occurs, which is evidenced by the significant decreasing of $\text{Hf}^{4+}-\text{O}^{2-}$ charge transfer luminescence and increasing of Eu^{2+} emission intensity with increasing Eu^{2+} doping concentration, along with the presence of similar excitation band for the Eu^{2+} doped and undoped $\text{BaHfSi}_3\text{O}_9$.

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