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**Charge Transfer Luminescence of Hafnates under Synchrotron Vacuum Ultraviolet Excitation**

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**Experimental**

**Materials synthesis**

Samples of undoped BaHf(PO$_4$)$_2$, BaHf(BO$_3$)$_2$, BaHfSi$_3$O$_9$ and Eu$^{2+}$-doped BaHfSi$_3$O$_9$ were prepared in powder form by using high temperature solid state reaction methods. BaCO$_3$ (99.9%, Aldrich), HfO$_2$ (99.99%, Grimen), (NH$_4$)$_2$HPO$_4$ (99%, Aldrich), H$_3$BO$_3$ (99.9%, Aldrich), SiO$_2$ (99.6%, Aldrich) and Eu$_2$O$_3$ (99.9%, Aldrich) were used as the starting materials. All undoped samples were calcined in air. For synthesizing undoped BaHf(PO$_4$)$_2$, a 2% excess of (NH$_4$)$_2$HPO$_4$ was used, then the corresponding starting materials were mixed, ground, and pre-calcined at 900°C for 4 hours followed by calcination at 1200 °C for 6 hours with intermediate grinding. For the undoped BaHf(BO$_3$)$_2$, a 2% excess of H$_3$BO$_3$ was used, then the corresponding starting materials were mixed and ground thoroughly, followed by pre-calcination at 600°C for 4 hours and 1250 °C for 6 hours with intermediate grinding. For synthesizing undoped and Eu$^{2+}$-doped BaHfSi$_3$O$_9$, Li$_2$CO$_3$ (~3wt.%) was used as a flux. The corresponding starting materials were ground thoroughly, then the obtained mixtures were calcined at 1400-1500 °C for 6 hours under a reducing atmosphere (H$_2$:Ar = 15:85) for the Eu$^{2+}$-doped samples and in air for the undoped sample.

**Characterization**

The phase purity of all samples was checked by using powder X-ray diffraction (XRD) analysis with a Bruker AXS D8 advanced automatic diffractometer operated at 40 kV and 40 mA with CuKα radiation (λ= 1.5418 Å ). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured at BL03A beamline of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The VUV spectra were recorded at the Beamline 03A at National Synchrotron Radiation Research Center in Taiwan. VUV excitation light from the high-flux beamline attached to the 1.5-GeV storage ring was dispersed with a 6-m cylindrical grating monochromator (CGM). The intensity of the VUV light is monitored with a gold mesh transmitting about 90% and recorded with an electrometer (Keithley 6512). The VUV synchrotron light transmitted through the gold mesh irradiated the sample, which was arranged at angles near 45° with respect to both the incident VUV source and the entrance slit of the dispersing monochromator. A Jobin-Yvon HR320 equipped with a 1200 lines/mm grating and a Hamamatsu R943-02 photomultiplier (PMT) were used to record the PL spectra. For measurement of PL excitation (PLE) spectra, the dispersive emission was monitored at selected band; in which, the
CGM beam line with a 450 lines/mm grating was scanned. All the PLE spectra were normalized with the spectral response curve of the CGM beam line.

**Schematic illustration for Hf⁴⁺-O²⁻ charge transfer (CT) luminescence and energy transfer from hafnate intrinsic emission to Eu²⁺**

Upon VUV excitation at 172 nm, the charge transfer absorption occurs as an electron transition from ligand O²⁻ 2p orbital to the metal ion Hf⁴⁺ empty 5d orbital. After electron transfer to Hf⁴⁺, the hole appears to be distributed over ligands around the Hf³⁺ ion. In the reverse process, the radiative recombination of electron at Hf³⁺ (formed after electron transfer) with the hole localized on O²⁻ gives rise to the observed charge transfer luminescence. In the meantime, due to the favorable spectral overlap between Hf-O CT emission and Eu²⁺ 4f-5d absorption, the photon from Hf-O CT luminescence has enough energy to excite Eu²⁺ from its ground 4f state to its excited 5d state. Subsequently, the Eu²⁺ at excited 5d state returns to ground state by giving 5d-4f emission. The whole process is illustrated in Scheme 1.

Scheme 1. Overall picture of Hf⁴⁺-O²⁻ charge transfer luminescence and energy transfer process in BaHfSi₃O₉:Eu²⁺ upon VUV excitation.