

Electronic Supplementary Information (ESI)

Charge Transfer Luminescence of Hafnates under Synchrotron Vacuum Ultraviolet Excitation

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Experimental

Materials synthesis

Samples of undoped BaHf(PO₄)₂, BaHf(BO₃)₂, BaHfSi₃O₉ and Eu²⁺-doped BaHfSi₃O₉ were prepared in powder form by using high temperature solid state reaction methods. BaCO₃ (99.9%, Aldrich), HfO₂ (99.99%, Grimen), (NH₄)₂HPO₄ (99%, Aldrich), H₃BO₃ (99.9%, Aldrich), SiO₂ (99.6%, Aldrich) and Eu₂O₃ (99.9%, Aldrich) were used as the starting materials. All undoped samples were calcined in air. For synthesizing undoped BaHf(PO₄)₂, a 2% excess of (NH₄)₂HPO₄ 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(BO₃)₂, a 2% excess of H₃BO₃ 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 Eu²⁺-doped BaHfSi₃O₉, Li₂CO₃ (~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 (H₂:Ar = 15:85) for the Eu²⁺-doped samples and in air for the undoped sample.

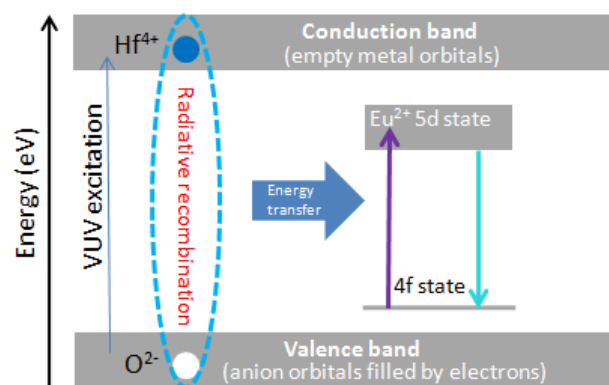
Characterization

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 CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). 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 $\text{Hf}^{4+}\text{-O}^{2-}$ charge transfer (CT) luminescence and energy transfer from hafnate intrinsic emission to Eu^{2+}

Upon VUV excitation at 172 nm, the charge transfer absorption occurs as an electron transition from ligand O^{2-} $2p$ orbital to the metal ion Hf^{4+} empty $5d$ orbital. 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. In the meantime, due to the favorable spectral overlap between Hf-O CT emission and Eu^{2+} $4f\text{-}5d$ absorption, the photon from Hf-O CT luminescence has enough energy to excite Eu^{2+} from its ground $4f$ state to its excited $5d$ state. Subsequently, the Eu^{2+} at excited $5d$ state returns to ground state by giving $5d\text{-}4f$ emission. The whole process is illustrated in Scheme 1.



Scheme 1. Overall picture of $\text{Hf}^{4+}\text{-O}^{2-}$ charge transfer luminescence and energy transfer process in $\text{BaHfSi}_3\text{O}_9\text{:Eu}^{2+}$ upon VUV excitation.