Cathodoluminescence of Mn4+-doped Lithium Hafnium Fluorides

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Cathodoluminescence of Mn^{4+}-doped Lithium Hafnium Fluorides

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The red-emitting Mn^{4+}-doped fluoride phosphors possessing a narrow red emission are a significant class of materials with high luminescence performance for light-emitting diodes applications. The fluoride hosts with central ion Si^{4+}, Ti^{4+}, Ge^{4+}, Sn^{4+}, Zr^{4+}, or Al^{3+} activated with Mn^{4+} or rare-earth (RE) elements have been well reported in the literature [1–7]. The Hf-based fluorides doped with RE elements have found application for radiation detection [5,7,8]. Here, we report the cathodoluminescence (CL) of Mn^{4+}-doped lithium hafnium fluorides. In a typical synthesis, a solution of LiF in methanol and aqueous $HfCl_4$ were prepared separately. The LiF was dispersed in methanol by sonication. The Mn^{4+} precursor K_2MnF_6 was synthesized by following the protocol reported elsewhere [9]. First, the required amount of K_2MnF_6 was dissolved in 1 mL 40% HF and quickly mixed with aqueous $HfCl_4$ solution. Then, the methanolic solution of LiF was added to the reaction mixture as soon as possible, stirred for 1 min, and precipitated with ethanol. The resulting solid product was separated via centrifugation and washed with ethanol several times. The final product was dried in an oven at 70 °C.

The phase purity and crystalline structure of the sample were examined by X-ray Diffraction (XRD). An example is shown in Figure 1(a), where all of the diffraction peaks match with the orthorhombic crystal structure of Li_4ZrF_8 with a space group *Pnma* (ICDD 04-011-1800) [10]. Since the X-ray scattering factor of Li is ignorable in the presence of heavy Hf, the structure is determined with neutron diffraction. There were no peaks arising from any secondary phases or impurities even after doping with Mn^{4+}. The morphology of the sample was analyzed by scanning electron microscopy (SEM). The SEM image Fig. 1(b) revealed the formation of aggregated near spherical nanoparticles with an average size of about 100 nm.

The CL properties of the Mn^{4+}-doped Li_4HfF_8 were investigated by xCLent CL spectrometer equipped on a JEOL field-emission JXA-8530F Electron Probe Microanalyzer (EPMA). To prepare the sample for CL, a small hole was drilled in previously prepared epoxy resin, and the material was filled into the hole and pressed using a hydraulic pellet press. The prepared sample was placed in the EPMA for analysis. The undoped host sample exhibited emission in the blue region with a maximum peak position at 490 nm, while the Mn^{4+}-doped sample showed a spectrum consisting of two peaks centered at 490 nm and 588 nm, respectively (Fig. 2). The 490 nm peak originates from the host emission, and the 588 nm peak originates from the Mn^{4+} emission. All the above results confirmed the successful doping of Mn^{4+} in the host for luminescence applications [8, 11].

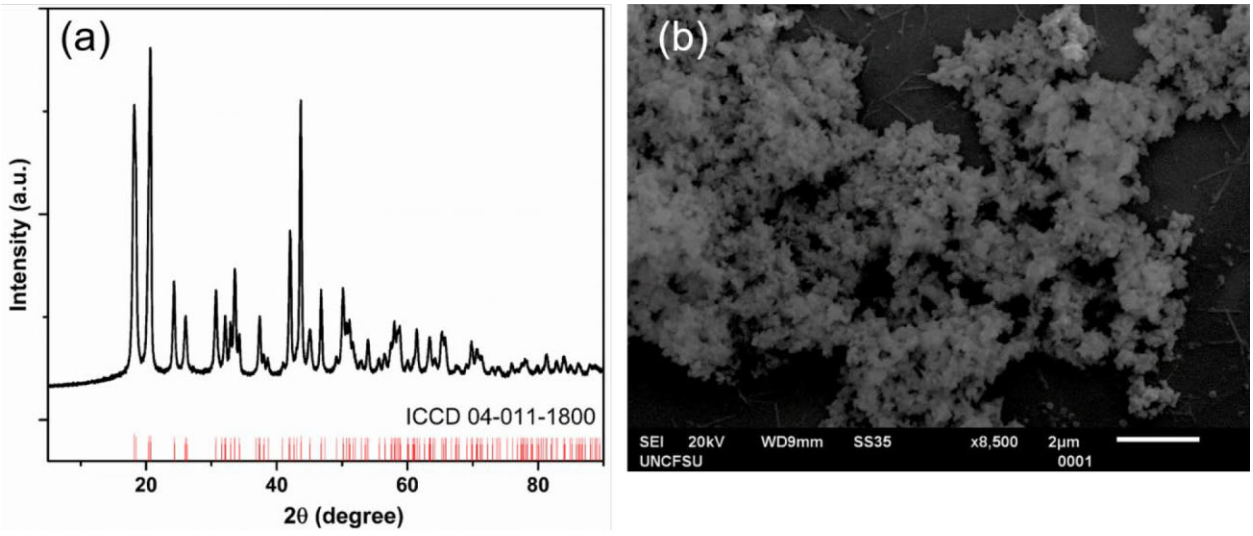

Figure 1. (a) XRD pattern and (b) SEM image of Mn^{4+}-doped Li_4HfF_8.

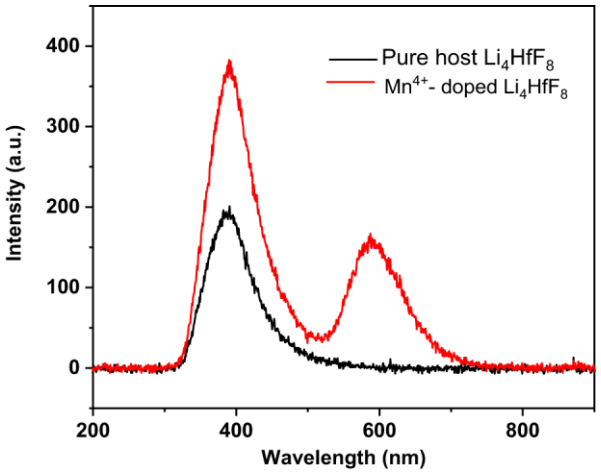

Figure 2. CL spectra of pure host and Mn^{4+}-doped sample.

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