Lutetium hafnates: From ceramics to OFZ-grown single crystals

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Heavy metal oxides, having high enough effective atomic numbers, belong to a group of inorganic materials that can fulfil the requirements for scintillators used in detection of high-energy photon radiation. Taking into account the state-of-the-art in the scintillators research, lutetium hafnates remain one of the last few poorly researched oxide materials, in both intrinsic and activated (for example, by cerium) scintillation. Within the Lu_2O_3-HfO_2 phase equilibrium, a gradual change from the cubic bixbyite-type Lu_2O_3 structure, via the cubic defect fluorite-type or pyrochlore-type solid solutions to the cubic hafnia stabilized by trivalent lutetium can be observed. In any case, the Lu_2O_3-HfO_2 system is represented by a few stoichiometric phases, pyrochlore $Lu_2Hf_2O_7$ and delta-phase $Lu_4Hf_3O_{12}$being the representatives. All described structures are characterized by a defect-based crystal structure, very high material density and very high melting point, the latter probably being the reason why these materials are not as explored as others.

In this work, we present the synthesis of ceramic rods of lutetium hafnium oxide, both undoped and doped by cerium ions, and their use at crystal growth by Optical Floating Zone (OFZ) technique. The ceramic rods were processed by multi-step vacuum assisted sintering starting from lutetia, hafnia and ceria. Even though the use of vacuum at temperatures around 1600 °C can ensure the reduction of cerium from Ce^{IV} to Ce^{III}, additional annealing in reducing atmosphere was also tested and its influence on the scintillation characteristics was established. Then, the rods were processed in an OFZ furnace producing single crystals. Because of the inherently low thermal conductivity of this defect-type oxide, we tested the use of either $Lu_2Hf_2O_7$ pyrochlore stoichiometry or $Lu_2Hf_3O_9$ congruent stoichiometry to see if cracking of the grown single crystals can be prevented.

The prepared ceramic samples and single crystals were characterized by the Raman spectroscopy and X-ray diffraction to evaluate the crystal structure. Within the rare-earth hafnates ($RE_2Hf_2O_7$) family, the Lu^{III}/Hf^{IV} ionic ratio predicts that the defect fluorite-type lattice is more stable; however, we detected that the observed crystal structure is also dependent on the synthesis route used. The radioluminescence spectra, as well as the absorption spectra were measured at room temperature and those of undoped and cerium-doped samples were compared. Additionally, photoluminescence (PL) excitation and emission spectra at both room temperature and a temperature of 10 K, together with corresponding PL decay kinetics, were collected to detect the allowed 5*d*-4*f* transition of Ce^{III} ions.

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