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Scintillating ceramics based on non-stoichiometric strontium hafnate

V. Jarý [a, *], P. Boháček [a], J. Pejchal [a], A. Beitlerová [a], B. Trunda [a], D. Pánek [b], P. Brůža [b], S. Kurosawa [c, d], A. Yoshikawa [c, e], M. Nikl [a]

[a] Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 1999/2, 182 21 Prague 8, Czech Republic
[b] Faculty of Biomedical Engineering, Czech Technical University in Prague, Sitna Square 3105, Kladno 272 01, Czech Republic
[c] New Industry Creation Hatchery Center (NICHe), Tohoku University, 6-6-10 Aza-Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan
[d] Faculty of Science, Yamagata University, 1-4-12, Kojirakawa-machi, Yamagata 990-8560, Japan
[e] Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan

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ABSTRACT

A set of non-stoichiometric strontium-hafnate ceramic samples was synthesized by the spark plasma sintering technique from powder precursors of optimized composition. The scintillation and optical properties of ceramic samples were investigated by means of time-resolved luminescence spectroscopy. We measured radioluminescence, photoluminescence excitation and emission spectra as well as luminescence decays excited by UV and soft X-rays, respectively. Multiple annealing was employed to optimize ceramic performance. Furthermore, optical properties of powder and ceramic sample of the same composition were compared. Application potential of studied ceramics in superfast imaging applications is discussed as well.

1. Introduction

Optical materials based on strontium hafnate, $SrHfO_3$ (SHO), have been studied since 1992 when Ce^{3+}-doped $SrHfO_3$ was patented as a scintillator [1]. Ce^{3+} 5*d* - 4*f* emission in SHO host is peaking around 400 nm with corresponding lowest absorption band at 310 nm and decay time below 20 ns. It has been shown in Refs. [2,3] that the temperature stability of the Ce^{3+} emission strongly depends on the Ce^{3+} concentration and surprisingly high amount of Ce^{3+}, up to 15%, can be incorporated in SHO structure. Besides the rare-earth doped SHO, undoped and non-stoichiometric SHO powders have recently been presented as interesting scintillating materials as well, mainly due to high density (7.64 g/cm^3), effective atomic number (60.2), absence of natural radioactivity, suitably positioned high intensity emission in near UV region (335 nm), which matches well the sensitivity of the conventional photomultipliers, and deeply sub-microsecond decay time (180 ns) [4]. It can therefore provide the base for a new class of efficient fast X-ray phosphors which are intensely searched for. Furthermore, it does not contain rare-earth elements whose price is dramatically increasing worldwide. Intrinsic nature of mentioned luminescence center responsible for the 335 nm emission was thoroughly discussed in Ref. [4]. Most probably the luminescence transition is due to a kind of charge transfer transition from oxygen anions (2p orbital) to hafnium cations (5d orbital) as these energy levels constitute the upper edge of valence band and lower edge of conduction band, respectively. The origin of this luminescence is therefore tentatively ascribed to the charge transfer transition in the Hf_{Sr} - O_{12} dodecahedron with a charge compensating Sr vacancy nearby [4]. Detailed studies of isostructural compounds based on non-stoichiometric zirconates of general formula $MeZrO_3$ (Me = Ca, Sr, Ba) have also been published recently [5,6]. Theoretical studies were employed as well to elucidate the formation of various centers in these non-stoichiometric compositions [7,8].

Due to extremely high melting point of SHO ($T_m > 2400$ °C) it is not possible to grow a single crystal bulk material. Several techniques, however, were applied to produce SHO in a powder form [9–13]. Recently, attempts to produce transparent ceramics of Ce^{3+}-doped SHO have been carried out, for example in Ref. [14]. Light output was estimated to be approximately 4000 photons/MeV. Although the material had a low transmittance, the sample could be prepared within roughly 10 h. Mg-codoping was also

* Corresponding author.
E-mail address: jary@fzu.cz (V. Jarý).

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considered in Ref. [15], where the highest light output was estimated to be ~5000 ph/MeV for the Al and Mg-codoped Ce^{3+}-$SrHfO_3$ pre-sintered at the temperature of 1400 °C. Mg admixture was suggested to play a role of sintering aid that stimulated the grain growth leading to the decrease of pore concentration and light scattering in the ceramics. The spark plasma sintering (SPS) is a very powerful sintering technique. It allows preparation of fully dense and fine-grained transparent ceramics at relatively low temperatures in a short period of time (see Ref. [16] and references therein). Ce-doped $SrHfO_3/SrAl_{12}O_{19}$ eutectics were grown also by the micro pulling down (μ-PD) method in Ref. [17]. The phase-separated scintillator fiber structure with fibers of around 3–4 μm diameter and 100–150 μm length was observed but the light yield reached only 300 photons/5.5 MeV alpha-ray and scintillation decay time was 26.4 ns (45%) with a slower decay component of 263 ns (55%).

Similar heavy Hf-based $Lu_4Hf_3O_{12}$ powder phosphors doped by RE-ions were also investigated as potentially interesting material group suitable for X/gamma -ray detection [18,19]. Fast $5d - 4f$ emissions of both Ce^{3+} and Pr^{3+} are, however, absent, which might be due to the positioning of the $5d^1$ level in the conduction band of the host.

Transparent ceramics, such as YAG:Ce [20], LuAG [21] and Lu_2O_3 [22], represent a promising class of polycrystalline materials for scintillator applications. By using transparent ceramics, not only the production costs can be greatly reduced, but also the activator concentration and homogeneity can be dramatically enhanced. Transparent ceramics have become alternatives to replace single crystals for scintillator applications, such as gamma ray spectroscopy and radiography. This paper presents optical and scintillation properties of novel interesting material concept based on spark-plasma sintering ceramics prepared from non-stoichiometric $SrHfO_3$ powder precursors.

2. Sample preparation and experimental techniques

Bohacek et al. have recently revealed that non-stoichiometric material of the formula $Sr_iHf_{2-i}O_{4-i}$, i = 0.8–0.95 shows a very intense emission under the X-ray excitation in near UV spectral range (Fig. 1) with reasonably fast decay time of about 180 ns at room temperature. Based on Bohacek's work [4] the powder sample of starting composition $Sr_{0.9}Hf_{1.1}O_{3.1}$ for optical ceramic preparation was manufactured by a multi-step solid state sintering procedure with the annealing temperature within 1100–1200 °C in the Institute of Physics, in Prague. The grain size of the prepared powders was on the order of several microns. SPS method in the Institute for Materials Research of Tohoku University was then used to produce the ceramic material using the machine DR SINTER (Fuji Denpa). The SPS ceramic samples platelets were prepared under the 100 MPa pressure and at four different temperatures (1600 °C, 1700 °C, 1800 °C, 1900 °C) in vacuum (few Pa) for 45 min. To restore their luminescence, these ceramic samples were repeatedly annealed in air for 6 h at 1185 °C and then studied. During annealing the samples were placed on a ZrO(2) ceramic plate - always with the same ("bottom") side in touch with the ZrO(2) base; the measurements were then carried out from both "upper" and "bottom", sides.

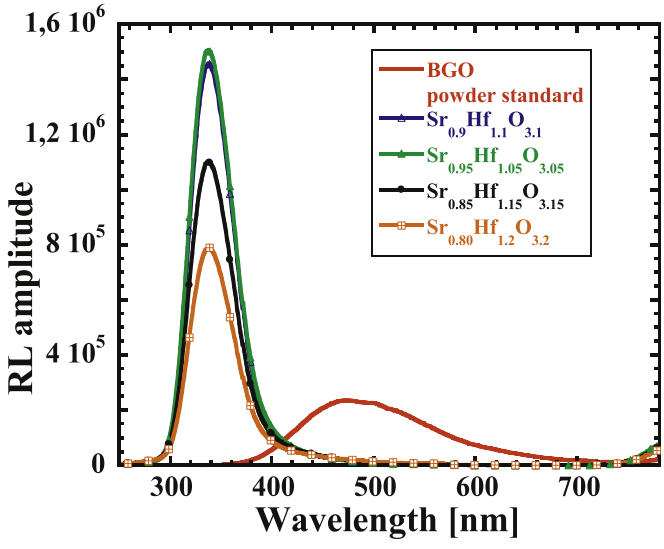

Fig. 1. RT X-ray excited emission spectra of powder $Sr_iHf_{2-i}O_{4-i}$, i = 0.8–0.95 (40 kV, 15 mA).

Room temperature (RT) radioluminescence (RL), photoluminescence excitation (PLE) and emission (PL) spectra and decay curves were measured by a custom-made spectrofluorometer 5000M, Horiba Jobin Yvon, using the steady state deuterium lamp (PL and PLE spectra), Mo X-ray tube (RL spectra) and nanosecond nanoLED pulsed light sources (fast prompt decay curves) as the excitation sources. Detection part of the setup involved a single-grating monochromator and the photon counting detector TBX-04. Measured spectra were corrected for the spectral dependence of excitation energy (PLE) and spectral dependence of detection sensitivity (PL). Deconvolution fitting procedure was applied to the decay curves to determine the true decay times (SpectraSolve software package, Ames Photonics). The scintillation efficiency of the studied samples was quantified by comparison of their RL intensities with that of $Bi_4Ge_3O_{12}$ (BGO) powder standard sample at 500 nm.

The scintillation decay under soft X-ray (SXR) excitation was performed using the nanosecond pulsed excitation source consisting of Ar plasma produced by short IR laser pulses (7 ns) in a gas puff target. The emitted radiation was filtered using a twin Ti filter of 0.4 μm thickness which resulted in a poly-monochromatic radiation with the photon energy in the spectral range of 350–450 eV. The light emitted from the sample passed through a monochromator (Jobin Yvon H20, France) and was detected by a fast photomultiplier (Hamamatsu R7056, Japan). The signal was amplified by a trans-impedance amplifier (Analog Devices AD847, USA) and recorded by a digital sampling oscilloscope (Agilent Infiniium DSO7104, USA). See Ref. [23] for further details.

3. Results and discussion

3.1. Materials characterization

RT RL spectra of several different $Sr_iHf_{2-i}O_{4-i}$, i = 0.8–0.95 powder samples considered as ceramic precursors are shown in Fig. 1. They consist of intense broad emission band peaking at around 335 nm as already mentioned in Ref. [4]. The origin of this luminescence is tentatively ascribed to the charge transfer transition in the Hf_{Sr} - O_{12} dodecahedron with a charge compensating Sr vacancy nearby, for details see Ref. [4]. The integral emission intensity of all samples (integrated in the 250–800 nm region) is compared to that of a standard BGO scintillator ($Bi_4Ge_3O_{12}$) in a crystal bulk form and for the optimal SHO composition reaches 120%, 170%, 220% and 210% of BGO for $Sr_{0.8}Hf_{1.2}O_{3.2}$, $Sr_{0.85}Hf_{1.15}O_{3.15}$, $Sr_{0.95}Hf_{1.05}O_{3.05}$ and $Sr_{0.9}Hf_{1.1}O_{3.1}$, respectively. Based on the radioluminescence properties of powders under consideration, composition of $Sr_{0.9}Hf_{1.1}O_{3.1}$ was chosen as the most suitable to be used for preparation of ceramics by SPS technique, see above.

A photograph of as prepared SPS ceramic samples platelets