SrHfO₃-based phosphors and scintillators

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ABSTRACT

The heavily Ce-doped SrHfO₃ (SHO) and the undoped non-stoichiometric SHO sample sets were prepared by solid state reaction in powder form and their luminescence spectra and decay kinetics were measured. Concentration quenching effects and thermally induced ionization of the Ce³⁺ excited states were followed and discussed in the former sample set. In the latter one new emission band at about 334 nm was found in Sr-deficient samples and temperature dependences of its emission intensity and decay times were studied in the detail. Room temperature decay time of about 180 ns and efficient and fast energy transfer from the host to the center of the 334 nm emission make this material promising candidate for X-ray phosphors.

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1. Introduction

Ce-doped SrHfO₃ (SHO) is known phosphor material which is attractive due to high density (7.56 g/cm³), low intrinsic radioactivity and fast response based on the Ce³⁺ 5d-4f emission [1]. It has been studied in recent years by several groups [2–6]. The Ce³⁺ doping at Sr²⁺ site induces coulombic disbalance in the lattice and the compensation mechanism has not been understood so far. The monovalent ion codoping was used to address this problem [5,6]. Apart from traditional solid state synthesis, the combustion synthesis [5,7] or sol–gel methods [4] have been used to prepare the powders. A few attempts were realized to prepare also optical ceramics [3,8] which indicate some practical potential of this material also in a bulk form.

Thermally induced ionization of the 5d₁ excited state of Ce³⁺ in SHO has been reported recently [9], which shows the onset of this degrading process somewhat below room temperature (RT). The onset of this process shifts with increasing Ce concentration to higher temperatures when the 0.1% and 5%Ce samples were compared. Recently, the Pb²⁺ dopant has been proposed for SHO host [10,11]: such a phosphor shows even higher efficiency, emission in near UV around 340 nm and about one order longer photoluminescence decay time of about 200 ns with respect to the Ce³⁺ doped material. Very recently the systematic study of the excitation and emission characteristics in the undoped stoichiometric SHO has been performed [12] which reveals quite several UV–VIS emissions ascribed to the exciton and defect centers. In the Pb or Ce-doped SHO the competition between these “intrinsic” centers and the dopants was demonstrated. At RT the energy transfer to the dopants is dominant.

In this paper we continue our studies focused on the heavily Ce³⁺-doped SHO. The processes of excited state ionization of Ce³⁺ center and concentration quenching are addressed as for their dependence on Ce concentration. New emission band at about 480 nm is found in Sr-deficient samples and temperature dependences of its emission intensity and decay times were studied in the detail. Room temperature decay time of about 180 ns and efficient and fast energy transfer from the host to the center of the 334 nm emission make this material promising candidate for X-ray phosphors.

2. Experimental

2.1. Sample preparation

For powder preparation the chemicals SrCO₃ (Johnson-Matthey Chemicals, grade 1), HfO₂ (Alfa Aesar, 99.95%) and CeO₂ (Koch-Light, 99.95%) were used. Powder samples were prepared by solid state reaction using a multiple step annealing procedures as follows (temperatures and duration in parenthesis are given): 500 °C (1 h) – 1100 °C (4 h) – 1170 °C (4–8 h). Two sets of samples were prepared, namely:

(1) Sr₀.₉₉Ce₀.₀₁HfO₃₀.₁, Sr₀.₉₅Ce₀.₀₅HfO₃₀.₅, Sr₀.₉Ce₀.₁HfO₃₁, Sr₀.₸₅Ce₀.₁₅HfO₃₁₅ (starting compositions) – these samples will be further denoted as Ce₀₀, Ce₀₅, Ce₀₁ and Ce₀₁₅, respectively.

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(2) five samples of undoped SHO with starting compositions Sr\text{Hf}_2\text{O}_4, \ 0.9 < i < 1.1.

2.2. Experimental techniques

The XRD spectra were measured on the diffractometer Huber in arrangement with plane wave, the radiation was produced by the X-ray generator Rotaflex with rotating anode (Cu) of the firm Rigaku. The radioluminescence (RL), photoluminescence (PL) and photoluminescence excitation (PLE) spectra and PL decay kinetics were measured at temperatures within 77 (10)–500 K, using the custom made 5000 M Horiba Jobin Yvon fluorescence spectrometer. Oxford LN Optistat and Janis closed cycle cryostats were used to achieve the desired temperatures. The steady state spectra were excited by deuterium lamp (PL, PLE) and an X-ray tube (RL, Seifert). Measurement of fast PL decay was performed under excitation by the hydrogen-filled nanosecond coaxial flashlamp using the time-correlated single photon counting method. In the ms time scale the decays were measured under excitation by microsecond xenon flashlamp and using the multichannel scaling method. PLE spectra and decays in VUV–UV region were measured at Superlumi station, HASYLAB, DESY, Hamburg [13]. All the spectra were corrected for the spectral dependence of the apparatus characteristics. True decay times were obtained using the convolution of the instrumental response function with an exponential function(s) and the least-square-sum-based fitting program (SpectraSolve software package, Ametec). Errors of calculated decay time values are typically few percent.

3. Results and discussion

3.1. Structural characterization

XRD spectra were measured for each sample. In the case of all heavily Ce-doped samples, XRD spectra showed minor content of CeO₂ and HfO₂ compounds. In the case of Ce0.15 sample, Fig. 1, three phases, namely, the orthorhombic SHO (ICDD Card No. 88-14), monoclinic HfO₂ (ICDD Card No. 34-104) and cubic CeO₂ (ICDD Card No. 34-394) were found. Phase analysis found for their contents (in wt%) the ratio 90:4:6, respectively.

In case of nonstoichiometric samples the XRD spectra show very minor content of HfO₂ and SrO for the Sr-deficient and Sr-rich samples, respectively. The detailed XRD spectra analysis of these samples will be reported elsewhere.

3.2. Heavily Ce-doped SrHfO₃

Radioluminescence spectra of the set of SHO:Ce samples are in Fig. 2. The Ce³⁺ emission at 410 nm [2–9] is accompanied by the band at about 335 nm and clear competition between these two bands is noted. Ce³⁺ emission intensity increases up to Ce0.1 sample. The origin of the 335 nm band is in question as it has not been observed in the stoichiometric undoped SHO [12]. Its spectral position is very close to that of Pb²⁺ center [10,11], but contamination by Pb ions is practically excluded in these samples (checked by ICP analysis). It is most probably related to the Sr-deficient SHO phase which is also supported by the residual content of HfO₂ compound in both the Ce-doped and Sr-deficient samples, see further in Section 3.2.

It has been noted in [9] that higher Ce concentration is beneficial for the shift of the onset of 5d state thermally induced ionization towards higher temperatures. Due to this observation a careful analysis of PL decays measured at RT was made, Fig. 3, for all the samples from Fig. 2. In fact, in all the samples but Ce0.01 the decay must be approximated by the sum of two exponential terms \[ I(t) = A_1 \exp(-t/T_1) + A_2 \exp(-t/T_2) + \text{background} \] + background. While the exponential tail of the decay curve characterized by the longer decay
time $T_2$ is defined by the transition characteristics of the Ce$^{3+}$ center itself, the distortion (acceleration) of the initial part of the decay points to an energy transfer or concentration quenching process. Due to heavy Ce doping the latter process can be a logical consequence. The relative weight (lightsum) of the faster component is calculated as $I_1 = A_1 T_1 / (A_1 T_1 + A_2 T_2)$ and can be used to evaluate quantitatively the distortion of the decay from a single exponential course, i.e. the intensity of concentration quenching effect. Such an evaluation was performed and the dependence of $I_1$ and $T_2$ on Ce concentration is shown in the inset of Fig. 3. In fact, one can see clearly increasing relative value of the $I_1$ with Ce concentration which points to increasing concentration quenching effect. It appears, however, relatively mild up to the Ce0.1 sample at least. The value of $T_2$ is increasing with Ce concentration as well, which indicates the shift of the knee of thermally induced ionization of 5d$_1$ state of Ce$^{3+}$ center towards higher temperatures [9].

The two effects described will have the opposite influence on the scintillation efficiency of Ce$^{3+}$-doped SHO. Consequently, an optimum Ce concentration must exist which seems to be close to that in Ce0.1 sample. It is consistent with the observed RL intensity dependence in Fig. 2. The decay time of the 335 nm band is of about 170 ns in all the samples.

TD of PL spectra of Ce0.05 sample has been already published under the direct excitation into 4f-5d$_1$ absorption band of Ce$^{3+}$ at 310 nm [9]. Flat dependence on the temperature was obtained until some 230 K with gradual decrease up to RT and steeper decrease at higher temperatures. Such measurement can be influenced by temperature dependent absorption coefficient of Ce$^{3+}$ 4f-5d$_1$ absorption band due to light collection from rather thin sample layer because of light scattering in the powder. Therefore, the same measurement was performed under band-to-band excitation at 200 nm, Fig. 4. However, rather different spectral pattern was obtained at the lowest temperatures, in which the spectrum is dominated by a broad band peaking at about 450 nm and the Ce$^{3+}$ emission at 410 nm appearing just like a shoulder, Fig. 4a. The former emission is completely quenched at about 200 K, while the Ce-related one increases up to approx. 350 K and becomes weaker again at higher temperatures. The integral of PL spectrum above 200 K is displayed together with the mentioned TD from Ref. [9] and clearly different behavior of the Ce$^{3+}$ emission intensity is noted for both excitation wavelengths. Though the TD course at 200 nm excitation can be influenced by an energy transfer host $\Rightarrow$ Ce$^{3+}$, the emission intensity decrease above 300 K is definitely less pronounced with respect to the other TD measured under 310 nm excitation. As the penetration depth in the case of 200 nm excitation is much smaller (absorption coefficient in the excitation region will be several orders higher respect to that in 4f-5d$_1$ absorption band of Ce$^{3+}$) and is estimated of the order of 1 $\mu$m, the mentioned above effect of temperature dependence of the 4f-5d$_1$ absorption coefficient could be indeed important. In other words, the true TD of the 410 nm emission of Ce$^{3+}$ will be above 300 K between two curves in Fig. 3.

To complete luminescence characteristics of the 450 nm emission band, its excitation spectrum and decay were measured at 77 K in Figs. 5 and 6, respectively. PLE spectrum shows three bands at about 410–420 nm, 270–280 nm and 220–230 nm and efficient excitation in the SHO band edge as well. The decay is dominated by fast component of about 6–7 ns decay time and somewhat slower possibly non-exponential tail is present as well. Small Stokes shift of a few tenths of eV, broad emission band and fast ns decay are typical for the $F^-$ centers in complex oxides, e.g. in Y$_3$Al$_5$O$_{12}$ [14], YAlO$_3$ [15,16], Lu$_2$Al$_5$O$_{12}$ [17] and Lu$_6$Hf$_5$O$_{12}$ [18] so that we ascribe the 450 nm emission to the $F^-$ center in SHO as well.

The mechanism of the Ce$^{3+}$ incorporation into SHO host in such high concentrations is worth to be discussed. According to the phase analysis, in the sample Ce0.15 there remains certain amount of CeO$_2$ (6 wt%) and of HfO$_2$ (4 wt%) separated from the SHO phase.

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Fig. 4. Temperature dependence of (a) PL spectra of Ce0.05 sample. Excitation at 200 nm, (b) integral of PL spectra for exc = 310 nm and 200 nm (in the latter for the temperatures above 200 K only).

Fig. 5. PLE spectrum of the 450 nm band at 77 K. Emission wavelength at 520 nm was chosen to reduce the effect of scattered light in the measurement of a powder sample, which does distort the measurement above approx. 440 nm.
3.3. Nonstoichiometric SHO

To complete further the luminescence characteristics and study possible influence of SHO stoichiometry, the set of several samples of varying stoichiometry, Sr$_{1-x}$Hf$_x$O$_{3-y}$, $0.9 \leq x \leq 1.1$ was prepared and characterized. PLE and RL spectra are in Fig. 7. The Sr-rich sample shows the 420 nm band which has been already reported in the stoichiometric SHO sample prepared by sol–gel method [12]. Its PLE spectrum shows the maximum around 210 nm just below the band-edge which is consistent with the trapped exciton and/or defect origin proposed in Ref. [12]. Very low excitation efficiency is noted above the gap within 90–170 nm. Below 90 nm the onset of electronic multiplication is evident. In the opposite nonstoichiometric limit, the Sr-deficient sample shows strikingly different luminescence spectrum dominated by the 334 nm band which is practically identical with that observed in Fig. 2. This emission is very efficiently excited in the band edge and above it as well, which points to efficient energy transfer to this center from SHO host. Another two excitation bands at about 221 nm and 270 nm, i.e. below the band-gap, point to the defect-origin of the 334 nm band.

Fig. 7. PLE and RL (excitation by X-ray, 40 kV) spectra of undoped SHO powders with varying stoichiometry.

TD of the 334 nm emission was measured within 77–500 K (see examples of spectra in the inset of Fig. 8) and the spectra were integrated to evaluate their temperature dependence, Fig. 8. Mild increase or temperature independent course is noted up to 320 K followed by the double-slope decrease where the steeper slope starts around 400 K.

PL decays of the 334 nm emission were measured under the excitation at 270 nm and decay times evaluated in the 10–500 K temperature interval, Fig. 9. Excellent single exponential decays were obtained through 2–3 orders of magnitude up to 400 K at least. Low temperature limit of PL decay time is 286 ns ($T = 10$ K) with the knee on the TD at about 50 K. Single slope of TD of decay times extends then up to 400 K followed by the steeper decrease of decay time values, see inset of Fig. 9. To get information about the speed of energy transfer from the host the decay of 334 nm band was measured in DESY under 270 nm and 110 nm excitations,

Fig. 8. Temperature dependence of the 334 nm emission band (PL spectra integrals), exc = 270 nm. In the inset the examples of the PL spectra at 77, 297 and 497 K are given which show approx. 110 meV high energy shift of the band within 77–497 K.
Fig. 9. PL decay time temperature dependence related to the 334 nm band under excitation in the lowest absorption/excitation band at 270 nm. Solid line is just to guide the eye.

Fig. 10. In the latter case only small build-up and slowing-down of the decay was obtained (decay time increased from 176 ns to 189 ns) and the relative signal level before the rising edge of the decay respect to decay amplitude is comparable for both excitations which means that under 110 nm excitation there is no considerably slower decay component underlying the measured decay curve in the 200 ns time window.

The obtained TD’s of emission intensity and decay time of the 334 nm band point to the two-excited-level scheme (so called three level model) frequently applied to model the TD of self-trapped exciton emission intensity and decay times in other complex oxides [19–21]. The onset of thermal quenching is indicated at about 400 K. Gradual increase of emission intensity within 100–200 K in Fig. 8 is not clear and needs further study. It could be caused e.g. by temperature dependence of the 270 nm absorption band or by other temperature dependent non-relaxed excited state characteristics.

To get more insight in the processes occurring in the excited state of the 334 nm emission we employed the measurement of the delayed recombination decay of this emission similarly as done in the Pr-doped LSO and VSO [22] or Ce-doped SHO [9] as well. The decay is measured at the same excitation/emission wavelengths, but in an extended ms time scale to monitor any delayed recombination processes arising due to the escape of electron from the excited state of luminescence center to the conduction band or any trap nearby and its return and radiative recombination at the center at later times. This technique proved very successful to detect thermally induced ionization of the luminescence center excited state and due to its purely optical character it can be applied also to powders as shown e.g. for LPS:Pr [23]. Temperature dependence of the delayed recombination decay integrals (first point which contains the prompt ms component is omitted in the integration) is given in Fig. 11. There is no immediate explanation of the step-like increase of the integral value within 120–320 K, but the nanosecond decay time values in Fig. 9 are of perfectly “single-slope” dependence within this temperature interval which excludes any additional effects occurring in the relaxed excited state of the center. Steep increase of the integral above 400 K is correlated with the onset of thermal quenching evidenced in TD of decay times and emission intensities in Figs. 8 and 9. Thus, the thermal ionization of the center is identified as one possible cause of the 334 nm band quenching.

It seems difficult to propose the nature of the emission center responsible for the 334 nm emission band basing on the present experimental data. As it is related to a defect and it is arising in a Sr-deficient SHO structure, the Sr vacancy should play a role in such a luminescent center creation. Great similarity is found with the exciton luminescence in tungstates or molybdates where the luminescence process occurs as a charge transfer transition in the oxygen group with possible participation of heavy divalent cation in the absorption transition, i.e. non-relaxed excited state of the center, in case of PbWO₄ see e.g. [24,25]. The relaxed excited state of the luminescence center in these materials (d-orbital of Mo⁶⁺ or W⁶⁺ ions) might be analogous to that in SHO [26,27]. However, further research is needed to provide a well-grounded hypothesis for the nature of the 334 nm emission center in Sr-deficient SHO.

4. Conclusions

Heavily Ce-doped SrHfO₃ phosphors and and the undoped non-stoichiometric ones were prepared by solid state reaction and characterized by several luminescence methods. In case of the Ce-doped
samples the highest radioluminescence intensity is obtained for Sr$_{0.9}$Ce$_{0.1}$HfO$_{3+0.1}$ composition. In PL decay the effect of concentration quenching and of the position of the onset of 5d$_1$ excited state ionization was demonstrated and discussed. New emission band at 450 nm was revealed with decay time of about 6–7 ns at 77 K and ascribed to the F$^+$ center.

Stoichiometry of SrHfO$_3$ appears to have a crucial impact on its luminescence properties. The Sr-rich sample shows the dominant emission at 420 nm, the RT excitation of which is most efficient just below the band edge at about 210 nm and efficiency of excitation above the gap within 90–170 nm is very low. The Sr-deficient SrHfO$_3$ shows new emission band at 334 nm, which is excited both below the gap at 270 and 220 nm and very efficiently also in the band edge and above the gap. Room temperature PL decays excited at 270 nm and 110 nm show very similar decay times of 176 ns and 189 ns, respectively, and no underlying slower component is noted in the latter case. It points to an efficient and fast energy transfer from the host to the center of the 334 nm emission. The onset of thermal quenching is found well above RT at about 400 K. Thermally induced ionization of the relaxed excited state of the emission center is found above this temperature as well and can be one of the reasons of the quenching process.

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