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Thermally-induced ionization of the Ce^{3+} excited state in SrHfO_3 microcrystalline phosphor

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ABSTRACT

We measured temperature dependences of emission spectra, prompt nanosecond decays and millisecond delayed recombination decays for the Ce^{3+} center in the SrHfO_3 (SHO) host. We characterized two samples with 0.1% and 5%Ce prepared by the acetate and citrate combustion and solid state reaction, respectively. The decrease of nanosecond decay times above approximately 220 and 260 K, respectively, is due to thermal ionization of $5d_1$ excited state of the Ce^{3+} center. Energy barrier of 300 meV, governing this process, is calculated for both the 0.1% and 5%Ce:SHO samples. Thermoluminescence glow curve measurement after X and UV (310 nm) irradiation at RT provides another support for the $5d_1$ excited-state ionization of Ce^{3+} in the SHO host.

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1. Introduction

The Ce^{3+} doped SrHfO_3 (SHO) microcrystalline phosphor has been studied in recent years by several groups [1–5] due to its elevated density (7.56 g/cm³) and effective atomic number which are favorable for X(γ)-ray imaging applications. Moreover, fast emission and scintillation response is enabled due to Ce^{3+} $5d_1$ –4f emission at 408 nm. Its photoluminescence and scintillation decay time values of 36 ns and 42 ns, respectively, were reported at room temperature (RT) [1,2]. The doping by Ce^{3+} at the Sr^{2+} site must introduce a coulombic disbalance requiring a compensation by either some point defects, or deviations from stoichiometry. Compensation mechanism is not well understood and codoping the host lattice is also used to solve the problem [4,5]. However, in our recent study where we compared the luminescence and scintillation characteristics of the Ce and Pb-doped SHO [6], at RT we found rather short Ce^{3+} photoluminescence decay time of about 15 ns. Similar values were obtained in the samples prepared by two different technologies (solid state reaction as well as acetate and citrate combustion) pointing to the decay time independence of the manufacturing technology. Such a significant difference with respect to published values in SHO host is not understood. One has to study the temperature dependence of Ce^{3+} decay time to obtain a true radiative lifetime at low temperatures and to reveal possible quenching or ionization processes in the $5d_1$ excited state level of Ce^{3+} , where especially the latter can occur in complex oxides when this level is close to the conduction band edge [7].

In this paper we report the Ce^{3+} $5d$ – $4f$ luminescence characteristics in the SHO host in a wide temperature range 77–500 K. Our goal is to monitor the presence of processes in the $5d_1$ excited state that can influence the Ce^{3+} decay kinetics and to discuss their origin.

2. Experimental details

Preparation of the samples by the acetate and citrate combustion as well as solid state reaction was described in recent publications [6,8]. In both cases the powders consist of grains of several microns. Photoluminescence characteristics were measured at the custom made 5000 M fluorometer Horiba Jobin Yvon. The H2 steady-state lamp was used as an excitation source for measurements of the spectra, while ns coaxial H2-filled and microsecond xenon flashlamps were used as excitation sources for fast and slow decay kinetics, respectively. Photon counting TBX-04 detector and single grating excitation/emission monochromator were used. Furthermore, excitation spectra in UV–VUV region were measured at Superlumi station in DESY using standard “integral”, “fast component” and “slow component” regimes with “all times”, “gate 0–5 ns” and “gate 150–190 ns” detector regime (time = 0 refers to the excitation pulse arrival). All spectra are corrected for experimental response and deconvolution procedure is used in the decay curve evaluation to extract true decay time values. Thermally stimulated luminescence (TSL) glow curves were measured from 20 to 460 °C using a linear heating rate of 1 °C/s. The emitted light was detected in photon counting mode by a photomultiplier (EMI 9635QB). In the case of wavelength resolved TSL measurements

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the emitted light was detected both as a function of temperature and wavelength by a double stage micro-channel plate followed by a 512 diode array. The detection range was from 200 to 800 nm, using a 140 lines/mm holographic grating. X-ray irradiations were performed by a Machlett OEG 50 87 X-ray tube operated at 30 kV.

3. Experimental results and discussion

The excitation spectra at 300 K and emission spectrum at 77 K related to Ce^{3+} are displayed in Fig. 1. The $4f-5d_1$ transition of Ce^{3+} is peaking at 307 nm and the host band edge at 200–210 nm is well visible. Interestingly, the efficiency of excitation in the $4f-5d_1$ transition and SHO band edge is comparable and almost no slow components are visible in the latter which points to fast and efficient energy transfer from the host to the Ce^{3+} center at RT. In the emission spectrum the sub-bands at about 380 and 415 nm are well resolved. They are due to the ground state doublet of Ce^{3+} and their separation of about 2300 cm^{-1} well matches the usual value of the $^2F_{5/2}$ and $^2F_{7/2}$ level splitting. It is also worth noting unusually large Stokes shift of 0.75–0.8 eV that can be estimated from the separation of peaks in the excitation and emission spectra.

Under excitation at 310 nm, the emission spectra were measured at various temperatures between 77 and 350 K (at least), the spectra were integrated and the obtained value taken as an integral intensity for each temperature, see Fig. 2. The onset of emission intensity decrease is about 220 and 260 K for 0.1% and 5%Ce doped SHO, respectively.

An example of normalized photoluminescence decay at 400 nm is presented for the 5%Ce sample at RT in the inset of Fig. 3. Very good single exponential profile is evident through more than three orders of magnitude and decay time of 17.4 ns is evaluated. Temperature dependences (TD) of calculated decay time values are reported in Fig. 3 for both 0.1% and 5%Ce samples. They somewhat differ in the low temperature limit (27 and 20 ns, respectively). Consistently with the emission intensity TD, cf. Fig. 2, the onset of temperature induced decay time shortening is shifted to higher temperature in the 5%Ce sample. Thus, only low temperature limit of the decay time value in 0.1%Ce sample is closer (but not equal) to the value 36 ns reported in [1]. TD of the decay times displayed in Fig. 3 can be approximated by a single barrier model in the

Fig. 1. Photoluminescence excitation ($\lambda_{\text{em}}=400\text{ nm}$, $T=300\text{ K}$) and emission ($\lambda_{\text{exc}}=310\text{ nm}$, $T=77\text{ K}$) spectra of 5%Ce:SHO sample. Excitation spectrum is measured in the integral, fast component and slow component regimes at Superlumi station, DESY.

Fig. 2. Temperature dependence of emission intensities (spectra integrals) in 5% and 0.1%Ce doped SHO under excitation at 310 nm.

Fig. 3. Temperature dependence of decay time values. Circles and squares are experimental data obtained by single exponential approximation of the decay ($\lambda_{\text{exc}}=310\text{ nm}$, $\lambda_{\text{em}}=400\text{ nm}$). Solid and dashed lines are the temperature dependences calculated from the model, see the text Eq. (3). The parameters of the fit $1/\tau_r$, w_0 , ΔE are $4.55 \times 10^7\text{ s}^{-1}$, $5 \times 10^{12}\text{ s}^{-1}$, 300 meV, and $5.1 \times 10^7\text{ s}^{-1}$, $1.5 \times 10^{12}\text{ s}^{-1}$, 300 meV, for samples with 0.1% and 5%Ce, respectively. In the inset an example of the decay at RT with the single exponential fit $I(t)$ to the data is shown.

following way. A rate equation for population $n(t)$ of the excited $5d_1$ state can be written as follows:

$$dn(t)/dt = -n \times (k_r + k_n), \quad (1)$$

with k_r and k_n being radiative and nonradiative transition rates from $5d_1$ state to the ground state, respectively. Specifically:

$$k_r = 1/\tau_r \text{ and } k_n = w_0 \times \exp[-\Delta E/kT], \quad (2)$$

where τ_r stands for the radiative lifetime of $5d_1$ state of Ce^{3+} , w_0 and ΔE are frequency factor and energy barrier, respectively, of above mentioned barrier transition corresponding to an escape of electron from $5d_1$ level, k is the Boltzmann constant and T is the absolute temperature. Therefore, the observed decay time τ at the temperature T can be written as:

$$1/\tau = 1/\tau_r + w_0 \times \exp[-\Delta E/kT] \quad (3)$$

The energy barrier 300 meV is obtained from the fit of Eq. (3) for both the 0.1% and 5%Ce samples (solid and dashed lines in Fig. 3). It is worth noting that the decays in the former sample exhibit some

distortion from the single exponential course and worse agreement with the model is obtained at the highest temperatures. This fact may reflect lower crystalline quality and/or some technology-specific defects nearby Ce^{3+} centers in the sample prepared by acetate and citrate combustion making the evaluation by Eq. (3) less reliable.

Similar temperature dependences of emission intensity and PL decay times in Figs. 2 and 3, respectively, may point to a classical thermal quenching of the $5d_1$ excited state of Ce^{3+} in the SHO host. However, thermally-induced ionization of the $5d_1$ excited state of Ce^{3+} or Pr^{3+} in complex oxides is another well-known process also causing the decrease of the photoluminescence lifetime [9]. It is usually detected by photoconductivity [10]. To monitor such a process in powders we have developed purely optical method based on the measurement of the delayed recombination decay [9,11,12]. In this experiment the excitation/emission wavelength is set the same as in the nanosecond decay measurement, but the time window is set up to a few tens of milliseconds. The excitation is accomplished by a low frequency (10–30 Hz) intense microsecond xenon flashlamp. Temperature dependence of the decay curve integral can, with a good sensitivity, indicate the escape of electron from the $5d_1$ state and its later return to radiatively recombine. An example of such decay at 287 K is presented in Fig. 4. In Fig. 5 the temperature dependence of integral of the delayed recombination decay (the most intense point of the decay amplitude is omitted) is shown for $5d_1$ – $4f$ emission transition of Ce^{3+} in 5% and 0.1%Ce samples. Though the dynamical range is limited, the net increase of the signal with the onset of its rapid increase placed at similar temperature as the onset of nanosecond decay time decrease in the TDs in Fig. 3 demonstrates an ionization of the $5d_1$ excited state of Ce^{3+} . In the powder sample the dynamical range of the process can be much smaller than that in the single crystal as recently shown for LPS:Pr [12,13]. Nonradiative recombination (in addition to radiative) of ionized electrons can probably occur more easily in lower quality powder sample (in Fig. 2 might be indicated by the decrease of emission intensity).

Additional proof of the $5d_1$ excited-state ionization of the Ce^{3+} center in SHO at RT was obtained by thermally stimulated luminescence. Namely, in the 0.1%Ce sample the TSL glow curves were measured after X-ray as well as UV (310 nm) irradiation at RT. Both glow curves feature similar pattern, see Fig. 6. This observation

Fig. 4. Delayed recombination decay at 287 K, $\lambda_{\text{exc}} = 310$ nm, $\lambda_{\text{em}} = 400$ nm of 5%Ce:SHO sample. True background level is obtained at the same experimental conditions without the sample and reflects the signal level due to the noise of the photodetector.

Fig. 5. Temperature dependence of the integral of the delayed recombination decay for both 0.1% and 5%Ce doped SHO, the same conditions as in Fig. 4. The arrows indicate onsets of the nanosecond decay time shortening observed in temperature dependences presented in Fig. 3.

indicates that the traps giving rise to TSL peaks after X-ray irradiation get populated also after UV illumination in the Ce^{3+} absorption band. Moreover, TSL emission spectra displayed in Fig. 7 evidence the radiative recombination of charge carriers at the Ce^{3+} center. Since Ce^{3+} is known to act as a hole trap, according to a simple TSL scheme, the traps corresponding to observed TSL peaks are electron traps. These traps can become populated after UV irradiation at 310 nm provided that the Ce^{3+} electron excited by irradiation from the $4f$ to the $5d_1$ state is subsequently thermally promoted to the conduction band.

The reason why the 0.1% and 5%Ce sample differ in thermal stability of the Ce^{3+} emission center, see Figs. 2, 3 and 5, remains unclear. If there is any tiny difference in the structure e.g. due to heavy Ce doping in the latter sample, it was not obvious from the routine XRD check performed for the phosphors prepared.

The characteristics of the Ce^{3+} center in SrHfO_3 and their interpretation presented here are consistent with those recently published for the Ce^{3+} -doped CaHfO_3 [14]. In this work the authors observe the onset of the nanosecond decay time shortening around RT. Based on appearance of slower tails in the nanosecond decay above RT they propose that the decay time shortening is due to

Fig. 6. TSL glow curve of 0.1%Ce:SHO after X-ray (30 kV, 10 mA) and UV (310 nm, 35 min) irradiations at RT. The high temperature rise corresponds to black body emission.

Fig. 7. Normalized TSL emission spectra of 0.1%Ce:SHO obtained by integration of wavelength-resolved TSL measurements in the temperature regions indicated in the legend. Emission peak around 3 eV corresponds to the $5d_1$ – $4f$ transition of Ce^{3+} . The signal increase below 2 eV in the spectra above 300 °C is due to black body emission.

the thermally-induced ionization of the $5d_1$ excited state of Ce^{3+} . The value of the energy barrier of the ionization process calculated in [14] varies within 0.28–0.39 eV depending on the value of frequency factor (w_0 in Eq. (3)), being thus similar to the value $\Delta E = 300$ meV calculated in the present work (cf. Fig. 3). Similar evaluation for other ternary hafnate or zirconate perovskites has not been reported so far, and the temperature dependence of the photoluminescence decay was not systematically studied in them. The Ce-doped $SrHfO_3$ and $BaHfO_3$ were studied in the form of optical ceramics [2]. The latter seems to provide lower light yield and the RT decay time around 25 ns. The Ce-doped $SrZrO_3$ sol-gel prepared powders were studied in [15], the position of the Ce^{3+} luminescence is 5–10 nm low energy shifted with respect to the $SrHfO_3$ host, the reported RT decay time is about 24 ns. The $5d$ – $4f$ emission of Ce^{3+} and Pr^{3+} in $SrTiO_3$ is completely quenched [16] presumably due to the positioning the $5d$ levels within the conduction band of the host. To summarize, the literature data for the Ce^{3+} emission characteristics in the hosts mentioned above are consistent and critically depend on the separation of the $5d_1$ excited state of Ce^{3+} from the bottom of the host conduction band.

4. Conclusions

We study photoluminescence spectra, nanosecond decay and millisecond delayed recombination decay in the Ce^{3+} doped $SrHfO_3$

host. Temperature dependences of both prompt and delayed decay characteristics provide an evidence of the thermally-induced ionization of the $5d_1$ excited state of Ce^{3+} in the $SrHfO_3$ host with the onset of the process within 220–260 K. In case of both 0.1% and 5%Ce doped samples the energy barrier of thermal activation, 300 meV, was calculated from the temperature dependence of the prompt, nanosecond decay time values. Detection of TSL signal after UV irradiation in the $4f$ – $5d_1$ absorption transition of Ce^{3+} at RT and similar glow curve shape after both UV and X-ray irradiations offers additional independent proof of the excited Ce^{3+} center ionization at RT.

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