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Photoluminescence properties of non-stoichiometric strontium zirconate powder phosphor

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ABSTRACT

Excitation and emission spectra and decay kinetics of non-stoichiometric strontium zirconate powder phosphor were measured in the 8–500 K temperature interval. Phenomenological model was applied to extract quantitative parameters of the excited state levels and nonradiative quenching pathways related to the luminescence centre. Delayed recombination integrals measurement was employed to investigate the occurrence of thermally induced ionization of the excited state of the emission centre. The nature of the emission centre itself is suggested. Suitability for phosphor and scintillation application is discussed.

1. Introduction

Strontium hafnate-based (SHO) materials have recently become of a great interest owing to their potential applications as scintillators. SHO doped by Ce^{3+} is known phosphor material attractive because of the high density, low intrinsic radioactivity and fast response due to Ce^{3+} 5*d*–4*f* emission at 400 nm with the room temperature photoluminescence (PL) decay time of about 15 ns. It was patented in 1992 [1] and repeatedly studied in literature [2–5] where the radioluminescence and PL characteristics of Ce^{3+} emission centre are discussed in the broad temperature and concentration interval. Trapping states and excited state ionization of the Ce^{3+} activator in the SHO were addressed in a very recent paper [6]. Due to its very high melting point (T_m > 2400 °C) SHO is not available in the single crystal form but most recently a preparation in ceramic form was published [5,7]. Based on the theory of sol–gel science, perovskite SHO hollow cuboidal particles with tunable sizes were rationally synthesized by templateless hydrothermal reactions in KOH solutions [8]. Intrinsic and impurity-induced emission bands and the Gaussian decomposition of radioluminescence spectra recorded at different temperatures in an undoped SHO are studied in great detail in [9] revealing quite several UV–VIS emissions ascribed to the exciton and defect centers. The novel concept of non-stoichiometric SHO powder phosphor was open in [2] where the luminescence characteristics are studied as a function of the composition parametr i in $Sr_iHf_{2-i}O_{4-i}$. Recently, the Pb^{2+} dopant has been proposed for SHO host [9,10]: such a phosphor shows even higher efficiency, emission in near UV around 340 nm and about an order of magnitude longer PL decay time of about 200 ns with respect to the Ce^{3+} doped material. The theoretical investigation of the phonon properties of SHO in its cubic phase is presented in [4] to understand the role of phonons in this system. Structural, electronic and chemical bonding properties of the (001) surface of cubic SHO have been investigated [11].

Strontium zirconate-based (SZO) phosphors have received attention as well. Nanocrystalline europium-doped $AZrO_3$ (A = Ca, Sr, Ba) were prepared by Pechini-type complex sol–gel method [12]. Very dense rare earth doped SZO:Ce scintillating transparent ceramics for medical imaging (positron emission tomography) was introduced in [13] having the emission at 430 nm under UV irradiation, with a short decay time. The intense red emission of Eu^{3+} in SZO nanocrystals with a size of about 10 nm synthesized by a simple sol–gel combustion method was observed in [14]. Tm^{3+}-doped SZO powders were prepared by the polymeric precursor method [15] where the ultraviolet–visible absorption spectroscopy and PL measurements are introduced. A strong violet photoluminescence was also found in the undoped powder or nano-crystalline samples of SZO [16,17]. In 2011, non-stoichiometric strontium zirconate bright phosphor was discovered [18]. The PL emission from SZO crystalline, quasi-crystalline, and quasi-amorphous samples, prepared by the polymeric precursor method, was examined by ab initio quantum mechanical calculations [19]. The optical properties in the core-level spectra of cubic SZO are calculated by the

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full potential linearized augmented plane wave plus local orbitals method [20].

In this work we investigate in detail PL properties of non-stoichiometric Sr-deficient SZO, which, to our best knowledge, has never been studied before in detail. It shows suitably positioned UV emission at 355 nm, medium fast room temperature (RT) PL decay time (170 ns) and yet reasonably high density (5.40 g/cm^3) and effective atomic number (37.8).

2. Experimental details

Photoluminescence spectra and decay curves were measured by the custom made Spectrofluorometer 5000 M, Horiba Jobin Yvon, using the steady state deuterium lamp (photoluminescence excitation spectra (PLE) in the 190–500 nm spectral region and photoluminescence emission spectra (PL) in the 200–800 nm spectral region) and microsecond xenon and nanosecond hydrogen pulsed flash lamps (photoluminescence decay curves) as the excitation sources. Spectra were corrected for instrumental effects and a convolution procedure was applied to the decay curves to determine true decay times (SpectraSolve software package, Ames Photonics). The Janis Instruments closed cycle refrigerator was used to control the sample temperature in the temperature region 8–500 K.

3. Results and discussion

Detailed study of structural properties and their impact on radioluminescence features of non-stoichiometric strontium zirconate was published in [18]. Based on this work the sample of $Sr_{0.85}Zr_{1.15}O_{3.15}$ composition is chosen here for further investigation. The studied sample of starting composition $Sr_{0.85}Zr_{1.15}O_{3.15}$ belongs to the samples which were prepared, according the sintering procedure described in [18], from high purity starting materials (ZrO_2: Merck. Optipur, $SrCO_3$: Johnson Matthey, grade 1). According to Table 1 in [18] the sample consists of two stable phases, SZO (90 wt.%) and ZrO_2 (10 wt.%), composition of the SZO phase corresponds to the formula $Sr_{0.96}Zr_{1.04}O_{3.04}$, keeping in mind that the photoluminesce properties studied in this paper are connected to this $Sr_{0.96}Zr_{1.04}O_{3.04}$ phase. To make it clear, we will always refer to this sample as non-stoichiometric SZO in this work.

RT PL (λ_{ex} = 203 nm – blue curve and λ_{em} = 265 nm – red curve) and PLE (λ_{em} = 357 nm – black curve) spectra of non-stoichiometric SZO are displayed in Fig. 1. PLE spectrum consists of the non-stoichiometric SZO band edge at about 210 nm and another band of unknown origin at 265 nm. PL spectra, both excited by 203 nm

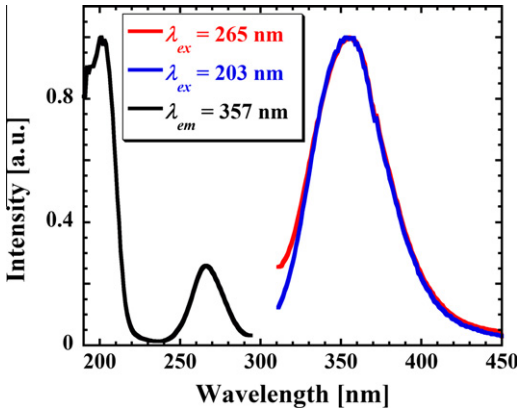

Fig. 1. RT PL (blue solid line under 203 nm excitation, red solid line under 265 nm excitation) and PLE (black solid line for 357 nm emission) spectra of non-stoichiometric SZO. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

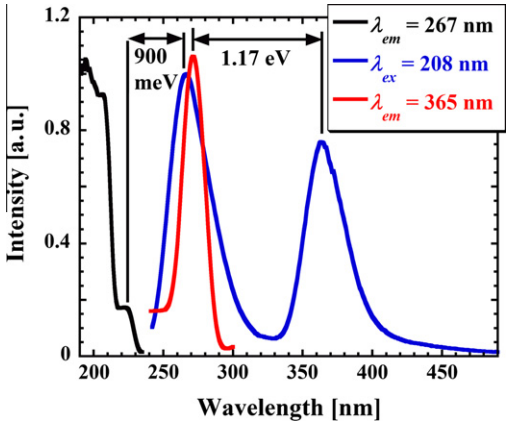

Fig. 2. PL (blue solid line under 208 nm excitation) and PLE (black solid line for 267 nm emission, red solid line for 365 nm emission) spectra of non-stoichiometric SZO recorded at 8 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and 265 nm radiation, feature one broad band with maximum 357 nm, whose description and origin are the subject of this study. The shape and position of the emission band coincide with that of X-ray excited [18]. Corresponding RT PL decay curve (λ_{ex} = 265 nm, λ_{em} = 357 nm) is single-exponential with the decay time of 167 ns.

PL (λ_{ex} = 208 nm – blue curve) and PLE (λ_{em} = 267 nm – black curve and 365 nm – red curve) spectra of non-stoichiometric SZO recorded at 8 K are shown in Fig. 2. Excitation in the band edge region (208 nm) gives rise to a new emission band peaking at 267 nm, which can be efficiently excited also slightly below the band edge at 223 nm (see Fig. 2 black curve) and based on similarity with SHO [9] we ascribe it to the self-trapped exciton. From the PLE and PL maxima of the exciton-related bands, Stokes Shift of 900 meV can be evaluated. Decay curve measured at 8 K (λ_{ex} = 225 nm, λ_{em} = 267 nm) is again single exponential giving the PL decay time of 313 μs. Furthermore, in the PL spectrum under the band edge excitation (see Fig. 2 blue curve) the UV band with maximum at 365 nm known from RT is present. Its PLE spectrum is formed by the band edge at around 205 nm (not shown in Fig. 2 for better clarity) and another band having the maximum at 271 nm, analogously to that at RT (see Fig. 1). Corresponding T = 8 K PL decay curve (λ_{ex} = 271 nm, λ_{em} = 365 nm) is single-exponential with

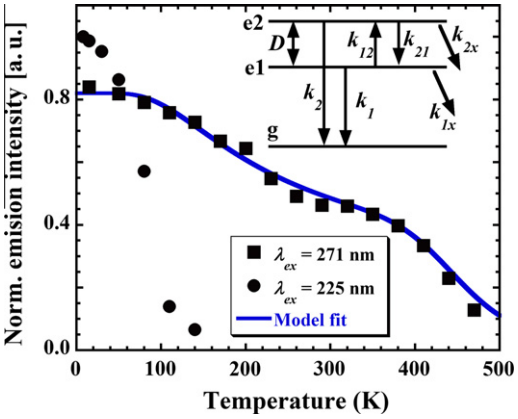

Fig. 3. Emission intensity temperature dependence of non-stoichiometric SZO under 225 nm (full circles – emission spectra integrated in the 250–350 nm spectral region) and 271 nm (full squares – emission spectra integrated in the 315–440 nm spectral region) excitation and the fit of the phenomenological model (see the text) to the data (blue solid line); model sketch in the inset (g – ground state, e1 – excited metastable state, e2 – excited radiative state) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).