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Optical Investigation of Sm doped ZrO₂

S. Lange¹, I. Sildos¹, M. Hartmanova², V. Kiisk¹, E. E. Lomonova³, and M. Kirm¹

¹Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

²Institute of Physics, Slovak Academy of Sciences, Dubravska cesta 9, 845 11
Bratislava 45, Slovak Republic

³Institute of General Physics, Russian Academy of Sciences, 117942, Moscow, Russia

E-mail: sven.lange@mail.ee

Abstract. A samarium doped polycrystalline ZrO₂ bulk sample was investigated for its phase composition as well as optical properties within the temperature range 6–300 K. From micro-Raman measurements the existence of tetragonal as well as monoclinic phase was confirmed. The emission spectrum of Sm³⁺ reveals drastic changes under excitation near the region of fundamental absorption. Combined excitation-emission spectroscopy (CEES) measurements reveal three different sites for the dopant ions to be present in the sample. Nature and excitation scheme of the three sites are discussed.

1. Introduction

Together with several other transition metal oxides zirconium oxide (ZrO₂) has been under investigation in the search for novel luminescent materials for some time now. Wide band-gap (>5 eV) and low phonon energies (<650 cm⁻¹) make it a promising host for doping with a wide range of luminescent impurities for operation at elevated temperatures. In combination with the high refractive index and high optical damage threshold this could lead to new luminescent materials of superior performance for applications like phosphor-converted LEDs, integrated optical amplifiers, laser hosts and other photonic materials.

Doping of ZrO₂ with various rare earth (RE) ions and the creation and study of intrinsic defects in the pure crystal have been reported by several authors already [^{1,2,3,4,5}]. Introduction of luminescent impurities, especially at high concentrations, required for several applications, markedly influences the phase content of zirconia. In addition, the nature of the host-sensitized excitation mechanisms leading to the emission of RE ions and intrinsic excitations is still a topic of ongoing debates [^{5,6}]. This is mainly because of the rather complicated electronic and phase structure caused by the dopants being able to stabilize zirconia in tetragonal and cubic phases in addition to the only naturally stable monoclinic phase at room temperature. In relation to the above in the current work we aim to investigate the phase structure, the distribution of the luminescent impurities and the luminescent properties of Sm-doped ZrO₂.

2. Experimental

The crystalline ZrO₂ containing 4 mol% of Sm₂O₃ were grown by the directional solidification of the melt using the direct microwave heating in a water-cooled crucible (SMT). The growth rate of the crystal was 10 mm/h. The cooldown of the crystal from 2000°C took place in steps with decreasing temperature gradients from 200–30°C/min. More detailed explanation of the technique can be found

elsewhere [7]. XRD study indicates the presence of nearly equal amounts of monoclinic and tetragonal phase (see Ref. [8] for in-depth description). In addition to standard XRD analysis the phase content and inhomogeneity of the sample was investigated via micro-Raman measurements. The measurements were conducted with a dedicated Renishaw micro-Raman setup with 514 nm laser excitations.

Combined excitation-emission spectroscopic (CEES) studies (eg. [9]) were applied to reveal different types of Sm centres in the sample. Individual PL spectra of CEES spectrum were measured using an Andor SR303i spectrograph equipped with an Andor ICCD detector and a Hamamatsu photomultiplier tube. A tunable multi-stage OPO (type NT 342/1/UVE) was used as the excitation source. PL spectra were corrected to the variable intensity of excitation source by recording the excitation spectrum of 623 nm line with a similar experimental setup having a continuous mode 150 W xenon lamp dispersed via MDR-23 monochromator as the excitation source. For low temperature measurements an UTREKS-type helium-bath cryostat was used.

3. Results

Micro-Raman measurements (spatial spot diameter $\sim 1 \mu\text{m}$) indicate a large inhomogeneity of the sample. Depending on the detection location on the sample we can see a variation of the Raman lines intensities corresponding to monoclinic (M) or tetragonal (T) phases (Fig. 1a,b). In addition, some photoluminescence (PL) of Sm^{3+} ions is excited. The PL line is situated at around $\sim 400 \text{ cm}^{-1}$ ($\sim 525 \text{ nm}$) to the red from the excitation wavelength of 514 nm.

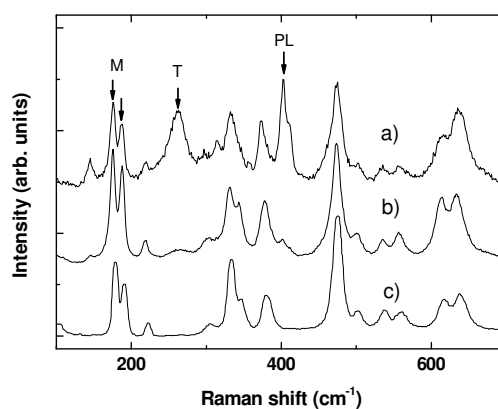


Figure 1. The micro-Raman spectrum of studied $\text{ZrO}_2:\text{Sm}^{3+}$ sample on two different locations (a) and (b) on sample (laser spot $\sim 1 \mu\text{m}$). A reference spectrum (c) of monoclinic ZrO_2 from reference [10]. Characteristic Raman lines of monoclinic (M) and tetragonal (T) phases as well as a photoluminescence (PL) band of Sm^{3+} are indicated.

For the measurement of the CEES spectra laser excitation in the interval of 210 to 480 nm was used. Chosen excitation range covers both indirect (210-300 nm) excitation near the fundamental absorption edge as well as direct (300-470 nm) excitation of Sm^{3+} through its f-f transitions. Luminescence spectra were registered in the interval of 550–750 nm, which corresponds to $^4\text{G}_{5/2} - ^6\text{H}_{5/2}$ manifold of f-f transitions of Sm^{3+} ions. General look of the results obtained at 6 K and room temperature (RT) are depicted in figure 2.

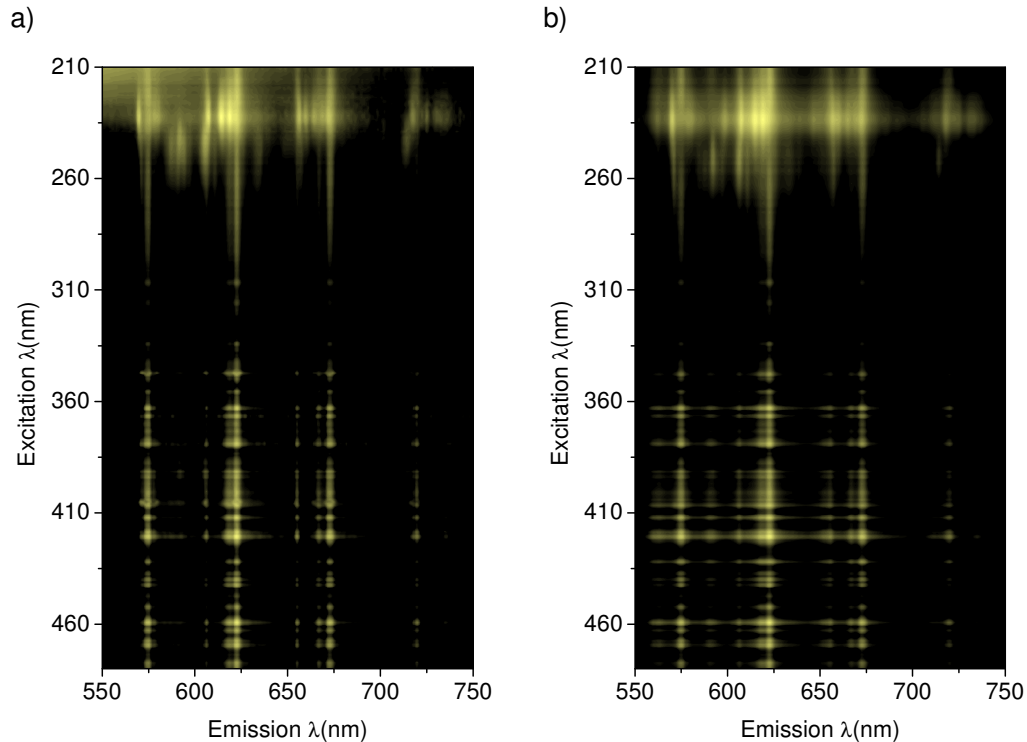


Figure 2. The combined excitation-emission spectra of Sm-doped ZrO₂ measured at 6 K (a) and RT (b). For coverage of the whole range of emission intensities a logarithmic scale is used.

From CEES spectra two distinct regions of Sm³⁺ excitation are revealed. At excitation wavelengths from 470 to 300 nm the directly excited PL emission characteristic to f-f transitions of Sm³⁺ ions is highly fluctuating in intensity. Below 300 nm the spectra represent a more uniform excitation region for the Sm³⁺ PL emission via indirect host mediated excitation of the ions.

The Stark splitting of the ⁴G_{5/2} to ⁶H_i (i = 11/2, 9/2, 7/2 and 5/2) emission lines of Sm³⁺ ion in tetragonal and monoclinic crystalline phases have been reported previously in [3,11]. By comparing low-temperature PL spectra derived from CEES spectrum at different excitation wavelengths we can suggest that in our sample Sm³⁺ ions both in the tetragonal and monoclinic crystal surrounding sites are indeed present (Fig. 3). Tetragonal phase is excited with varying intensity over the whole measured excitation wavelengths range from 210 to 480 nm (Fig. 4). Monoclinic sites are excited prevalently in noticeably smaller band centered at ~235 nm (Fig. 4). A third, yet unknown crystalline surrounding is presented by the additional PL lines at excitation near 240 nm. The latter maximum shifts to 250 nm at RT (Fig. 4b).

At 6 K a broad-band emission in the blue region of the PL spectra appears at excitation wavelength close to ZrO₂ fundamental absorption edge at 210 nm (Fig. 3a). This defect related emission is totally quenched at RT [12].

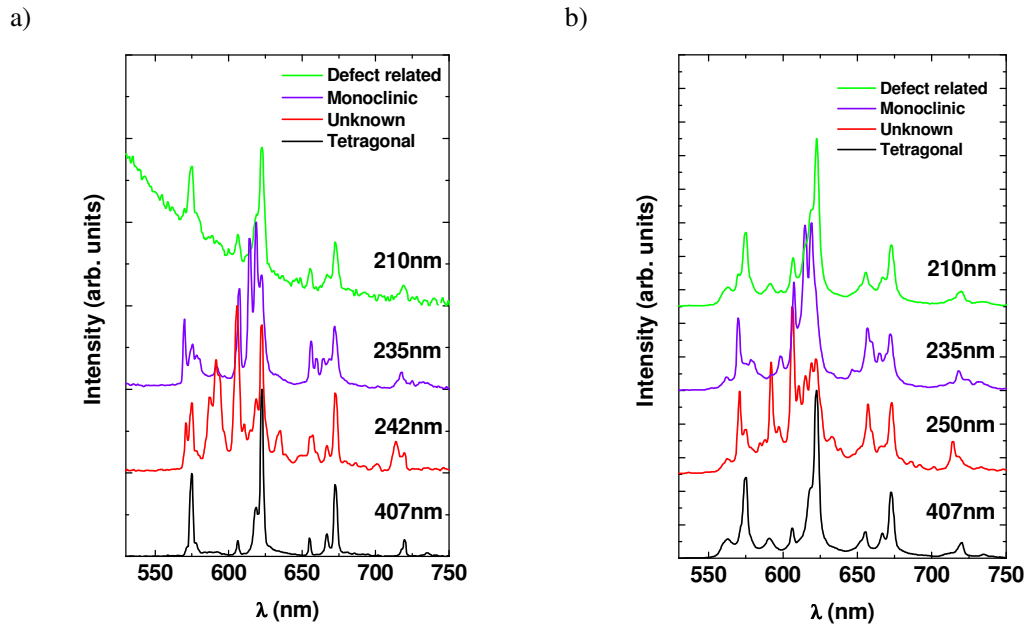


Figure 3. Sm^{3+} emission spectra at tetragonal, monoclinic and unknown sites of ZrO_2 at different excitation wavelengths. Measured at 6 K (a) and RT (b), respectively.

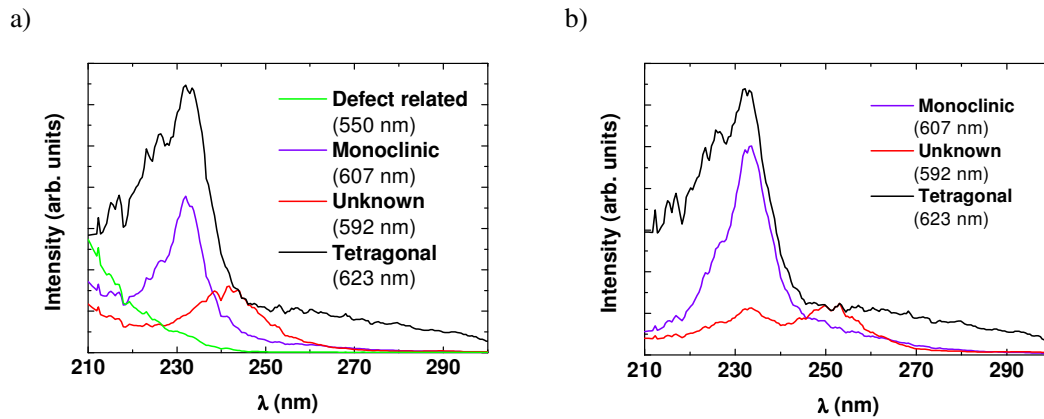


Figure 4. Excitation spectra of the Sm^{3+} emission in tetragonal, monoclinic and unknown phases of ZrO_2 at 6 K (a) and RT (b).

The PL decay curves of the three sites of Sm^{3+} have different behaviours (Fig. 5a). In tetragonal site the decay is nearly independent of temperature. Non-exponential behavior can be modelled fairly well by assuming an energy transfer to randomly distributed acceptors via multipolar interaction [13]. According to this model the PL decay can be described by the following equation:

$$I(t) = A \exp \left[-\frac{t}{\tau_{\text{rad}}} - \Gamma \left(1 - \frac{3}{s} \right) \frac{C}{C_0} \left(\frac{t}{\tau_{\text{rad}}} \right)^{\frac{3}{s}} \right], \quad (1)$$

where τ_{rad} represents the radiative lifetime, C is the concentration of the acceptor species, C_0 is a critical concentration corresponding to the rate of energy transfer equal to the radiative decay rate, and $s=6, 8$ or 10 depending on the type of interaction. Best fit (with $\tau_{\text{rad}} \sim 3.5$ ms) was achieved for $s=8$ characteristic of dipole-quadrupole interaction.

At 6 K the Sm^{3+} emission decay in monoclinic site is essentially non-exponential and has a prolonged tail. The decay profile for the unknown site occurred to be quite strongly temperature dependent. The decay curve is evidently non-exponential at RT but leads to the appearance of a well pronounced exponential part at 6 K (Fig. 5b).

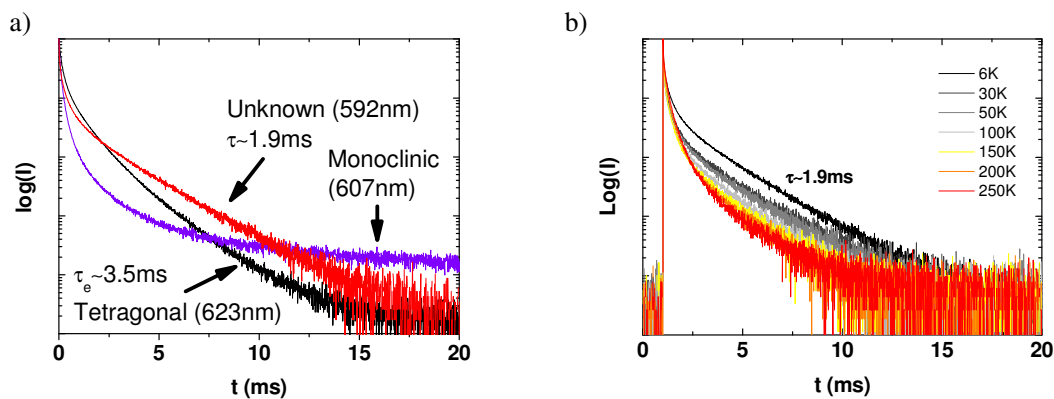


Figure 5. PL decay curves of Sm^{3+} ion emission in different surroundings of ZrO_2 matrix, measured at 6 K (a); temperature dependence of the PL decay curves for the of Sm^{3+} in the unknown site of ZrO_2 (b).

4. Discussion

According to Garvie and Nicolholson [14] the relative amount of monoclinic phase in mixed monoclinic/tetragonal ZrO_2 can be derived from the following empirical equation:

$$C_m = \frac{I_m^{179} + I_m^{190}}{I_T^{264} + I_m^{179} + I_m^{190}} \quad (2)$$

Here the different terms denote integral intensities of the Raman lines at indicated Raman wavenumbers. According to eq. (2) the Raman signal (Fig. 1) suggests that the phase-mixed sample has different surroundings present ranging from mixture of tetragonal ($C_t=52\%$) and monoclinic ($C_m=48\%$) phases to a lesser amount of almost totally monoclinic locations ($C_m=98.6\%$).

The presence of comparable amounts of monoclinic and tetragonal phases in many parts of the crystal leads to a large phase boundary area being present. The latter can be the cause for the emission from the unknown site in the CEES spectrum.

The difference of surroundings for the dopant ions cause three different routes of excitation for Sm^{3+} ions in the respective sites. The most prominent is the presence of the tetragonal phase over the whole excitation range from 210 to 480 nm. Above 250 nm where no other sites are excited the excitation is achieved dominantly via direct absorption of photons by Sm^{3+} ion 4f shell electronic transitions. The luminescence decay here is temperature independent and is shortened probably by a cross-relaxation between neighbouring Sm^{3+} ions due to their relatively high concentration (4 mol%).

The luminescence characteristic of the monoclinic phase is present only when excited into a band peaking at 235 nm (at both RT and 6 K) coinciding with the exciton absorption [5]. The long-lasting decay of the PL indicates a migration of the host electronic excitations prior to the energy transfer to the PL centre [15]. Similar behavior was noticed for Sm^{3+} in TiO_2 matrix.

We propose that in the phase boundary regions in the crystal where the third unknown sites of Sm^{3+} are present yet another route of excitation is prevailing. At 6 K the excitation is taking place probably from a defect donor level slightly lower in energy than the excitonic states. Due to the exponential nature of the decay we can conclude that the excited charge carriers are transferring the excitation to the Sm^{3+} ions relatively fast and no long-lasting migration is taking place (compared to monoclinic phase). At RT thermally induced relaxation processes cause the decay to become non-exponential and shortened and also lead to the appearance of another excitation peak close to the exciton absorption band (~235 nm). We suggest that it could be an indication that a donor level from the monoclinic phase has been opened for Sm^{3+} ion excitation via temperature assisted multiphonon relaxation. The existence of such possibility also suggests that the unknown phase must spatially be placed close to monoclinic phase where noticeable charged carrier migration was detected in PL decay curve. Additional spatially resolved Raman measurements are needed to confirm this.

5. Conclusion

Based on micro-Raman study it is inferred that the highly Sm-doped polycrystalline zirconia produced by the scull-melting technique contains nearly equal amounts of micrometer-scale distributed monoclinic and tetragonal phases of ZrO_2 . However, from the luminescence measurements it is concluded that the essential part of Sm^{3+} emission originates from the tetragonal phase with a clear indication of cross-relaxation in the decay kinetics. A lesser amount of active ions are situated in the monoclinic phase and appear to be preferentially host-sensitized with the excitation mediated by excitons. The third site revealed by CEES might be related to the boundary region of the two phases and can at RT partly be excited by charged carriers from monoclinic phase.

6. Acknowledgements

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