OPTICAL INVESTIGATION OF Sm-DOPED ZrO_2

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Introduction

- Wide band-gap, high refractive index, good mechanical strength and high optical damage threshold are in particular the properties rendering zirconium oxide (ZrO_2) rather interesting material for various applications such as laser cavities, optical coatings, gas sensors or insulating layers in semiconductor devices. Low phonon energies (<400 cm^{-1}) and wide band-gap (5.85 eV) simultaneously make ZrO_2 especially promising host for optically active dopants and defects [1-4].

Motivation of the work

- Revealing the different optically active sites for Sm^{3+} in ZrO_2.
- Investigate the possibility of determining the phase composition of Sm doped ZrO_2 by using combined excitation-emission spectroscopic studies (CEES).

Sample & experimental

- Bulk ZrO_2 sample doped with Sm_2O_3 salt (4 mol%), prepared by using the directional solidification of melt technique [5].
- Photoluminescence (PL) was excited with tunable OPO system NT342/1/UVE. PL spectra were recorded with spectrograph SR303i (Andor) equipped with air-cooled ICCD detector (Andor).

Results

- Three different type of sites can be distinguished for Sm^{3+} ion in ZrO_2 matrix (Fig. 3). The excitation maxima for the different sites (denoted as "unknown", monoclinic and tetragonal) are observed at: 242nm, 235nm and several absorption lines in the spectral range 300-480nm belonging to the direct f-f transitions of Sm^{3+}(Fig. 3,6).
- At 6K the photoluminescence related to the defect band of ZrO_2 crystal can be seen while exited with 210nm(Fig. 2a). This band disappears at RT (Fig. 2b).
- Decay curves of Sm^{3+} ion photoluminescence sites have different shapes (Fig. 4). For monoclinic site it is strongly nonexponential and has very long lasting tail (up to hundreds of milliseconds). For tetragonal site the profile is also nonexponential but can be easily approximated with multipolar interaction model[6] giving a radiative lifetime of ~3.5ms. For the unknown site the decay is almost single-exponential (τ~1.9ms) and becomes nonexponential by increasing the temperature (Fig. 5).

Conclusions

- CEES proved to be informative to distinguish different sites of emitting Sm^{3+} impurity and polycrystalline structure of ZrO_2:Sm^{3+}.
- Three crystalline surroundings for Sm^{3+} impurity in ZrO_2 are revealed. They are identified as tetragonal-, monoclinic- and a unknown phase [1,7].
- For each identified phase a specific route for Sm^{3+} excitation was found.
  - In tetragonal phase Sm^{3+} is excited mainly through f-f absorption and exhibits a nonexponential decay. Latter is caused by multipolar crossrelaxation between neighbouring ions leading to shortened radiative decay profile (Fig. 4).
  - In monoclinic phase Sm^{3+} is excited indirectly via excitonic absorption of ZrO_2 host (Fig. 6a,b). Pronounced long decay tail (Fig. 4) indicates to diffusion limited excitation path where charge carriers migrate to Sm^{3+} ion prior to energy transfer.
  - Sm^{3+} in the unknown crystal surrounding is mainly excited through some defect level situated slightly lower in energy compared to the excitonic absorption (245nm)(Fig. 6a,b). Temperature-caused shortening of the decay profile is most likely due to thermally induced non-radiative relaxation of the Sm ion. Increase of temperature also opens up phonon assisted relaxation channel from excitonic band to donor defect level leading to increased absorption from exciton states at RT.

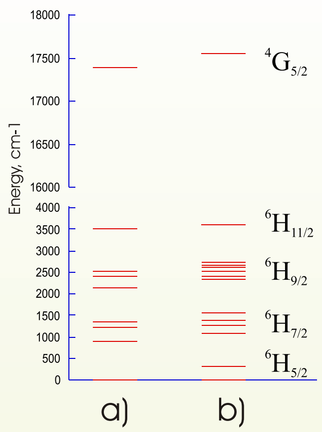

Fig.1. Scheme of Sm^{3+} energy levels for a) tetragonal b) monoclinic sites in ZrO_2(extracted from Fig. 2).

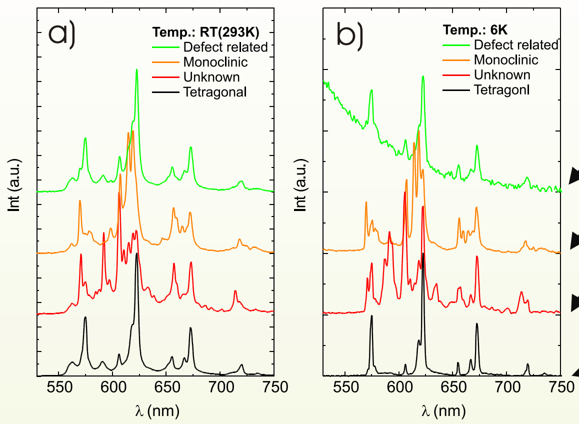

Fig. 2. Photoluminscence spectra of Sm^{3+} ion f-f emission corresponding to different sites in bulk polycrystalline ZrO_2 at a) RT and b) 6K respectively.

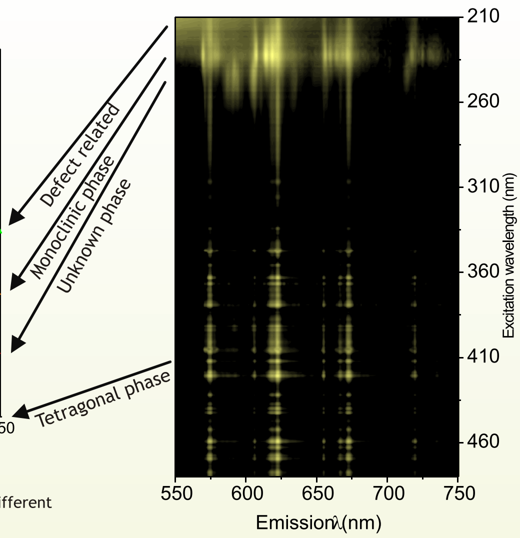

Fig. 3. Combined excitation-emission spectrum(CEES) of ZrO_2Sm^{3+} at 6K. Intensities in logaritmic scale for better overview.

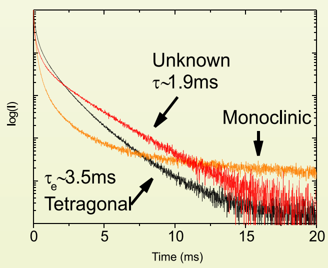

Fig. 4. Photoluminscence decay kinetics for the Sm^{3+} ion in different crystal phases of ZrO_2 at 6K.

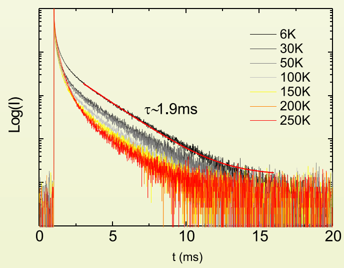

Fig . 5. Temperature dependence of the Sm^{3+} photoluminescence decay for the unknown phase in ZrO_2.

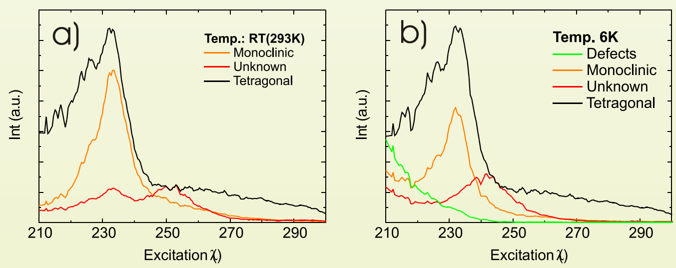

Fig. 6. Excitation spectra of Sm sites in tetragonal, monoclinic and unknown phases at a) RT b) 6K. For comparison the ZrO_2 related defect band excitation spectrum is added in b.

Acknowledgements

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