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## **SYNTHESIS AND INVESTIGATION OF THE PROMISE LUMINESCENCE MATERIALS**

Luminescence in rare-earth-doped systems has great interest due to its broad applications for phosphors, in solid-state lightning, for di-ode and visible lasers, display devices, for solar cell, as labels of bio-molecules, etc. Among different host matrix like single crystals, nanoparticles, glass and glass ceramics luminescence materials based on crystalline ceramics with pyrochlore/fluorite structure can be prospective matrix for efficient up-conversion. Pyrochlores have the general formula  $A_2B_2O_7$ , where A is a larger divalent or trivalent cation, in particular a rare earth elements, while B is a smaller tetravalent cation, typically Ti, Zr, Hf, Sn etc. In pyrochlore structure, cation A is eight-coordinated and located within a distorted cubic coordination polyhedron, and cation B is six-coordinated and being located in octahedral sites. The stability of these compounds is determined by the ratio of the radii of cations,  $r_A/r_B$ . If the greater the difference of A and B cations radii the more ordered the pyrochlore structure. When cations A and B have similar ionic radii and radius ratio is below 1.46 defect-fluorite structures are formed, in which the A and B cations are randomly distributed and the oxygen vacancies are disordered on the anion sublattice. If this ratio exceeds 1.78 the monoclinic structure will form [1–2]. Among wide range of pyrochlores,  $La_2Zr_2O_7$  based materials are employed in a variety of different applications thanks their interesting thermal and catalytic properties.  $La_2Zr_2O_7$  materials have huge potential application value as suitable phosphor matrix [3]. The present paper contains data on lanthanum zirconate ceramics distinct for their high-intensity luminescence.

For the synthesis of lanthanum zirconate ceramics sol-gel approach was used. Chemically pure  $Ln(NO_3)_3 \cdot xH_2O$  ( $Ln = La, Er, Yb$ ), zirconiumoxy-nitrate  $ZrO(NO_3)_2 \cdot xH_2O$  and ammonia were used for gel formation. Prepared gel was dried, calcined in air at  $800^\circ C/4h$ , ground and pressed into discs of about 1 mm thickness. The discs were fired in an electric furnace using heating ramp of  $10^\circ C/min$  up to  $1100–1500^\circ C$  with annealing time of 3 h. The samples were labeled as 0.01; 0.02; 0.05; 0.10. The label corresponds

to the Er<sup>3+</sup> concentration (in at.% by La ions) at constant concentration of Yb at the level of 0.02 at.% by La ion.

Diffractometer STOE Theta/theta with CoK $\alpha$  radiation source was used for X-ray diffraction (XRD) measurements. Diffraction angles were set in the range from 10 ° to 100 ° with a step width 0.020°. The DICVOL06 software from FULLPROF package was used for the calculations of lattice constants. The Williamson-Hall method was used for calculations of coherent scattering region (CSR) size and microstress values.

The excitation and emission fluorescence spectra were recorded using Fluorolog FL3-21 spectrometer (Horiba, France) equipped with PMT (R928) detector for visible and InGaS detector for NIR spectral range, respectively. The Xe-lamp (450 W) and 980 nm diode laser (SDL-980-LM-2500T laser, Shanghai Dream Lasers Technology, Co. Ltd.) with adjustable output power (0–2.5 W) were used as an excitation source.

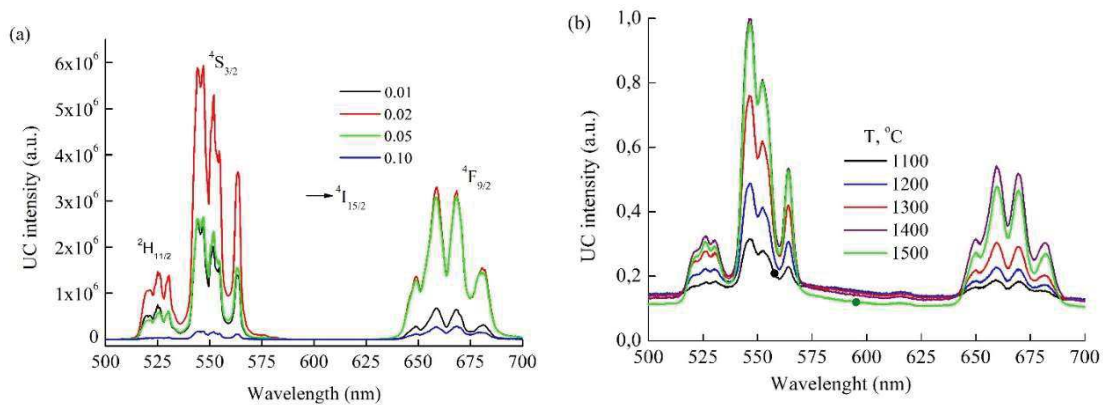
The XRD patterns of the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>:Er<sub>0.01</sub>Yb<sub>0.02</sub> ceramics obtained by heat treatment at 1100–1500 °C as well as for Er<sub>x</sub>Yb<sub>0.02</sub>LZ (x= 0.01; 0.02; 0.05; 0.10) ceramics obtained at 1400 °C it was found that all reflections correspond to the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> phase (96-200-2249). The calculated cell parameters for the studied are listed in Table 1.

**Cell parameters and crystalline size of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>:Er<sub>0.01</sub>Yb<sub>0.02</sub> ceramics obtained at different temperatures**

Temperature, °C]	a=b=c, Å	Crystallite size, Å	Microstrain, %
1100	10.79072	230–245	0.4–0.6
1200	10.79002	255–270	0.3–0.5
1300	10.78859	390–400	0.2–0.4
1400	10.78512	440–480	0.2–0.3
1500	10.78388	460–480	0.2–0.3

Increasing the temperature from 1000 °C to 1500 °C does not reveal a change of phase composition, however, leads to an enhancement of the peak intensities and narrowing due to the improvement of the crystalline structure. The crystalline size parameter for the investigated samples changes from 230–245 Å to 460–480 Å at increasing the annealing temperature from 1100 to 1500 °C indicating a better crystallization that correlates well with density of ceramics.

The calculated microstress values for samples obtained at 1100 °C and 1500 °C are 9.53·10<sup>-6</sup> and 7.9·10<sup>-6</sup> respectively. These points on the improvement of the crystalline structure at rising annealing temperature due to the decreasing different kinds of defects and connected with increasing emission intensity with annealing temperature (fig. 1).



**Figure 1 – Up-converted luminescence spectra (a) of  $\text{La}_2\text{Zr}_2\text{O}_7:\text{Er},\text{Yb}$  ceramics prepared at 1400 °C and evolution UCL spectrum of  $\text{La}_2\text{Zr}_2\text{O}_7:\text{Er}_{0.01}\text{Yb}_{0.02}$  with the annealing temperature (b)**

The emission in the green region at 523 nm and 543 nm is related to the  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  and  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  transition of  $\text{Er}^{3+}$  ions respectively; red emission in the 655–680 nm range is related to the  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  transition of  $\text{Er}^{3+}$ . With the increase of temperature, luminescence intensity remains near the same for the green region with a slight reduction for the  $\text{Er}_{0.1}\text{Yb}_{0.02}\text{LZ}$  ceramics. The increase of the  $\text{Er}^{3+}$  content in obtained ceramics results in the proportional increase of red emission. RGB colour coordinates indicated that average emitted colour induced by up-conversion changed in the range of green to yellow emission, from ~550 nm towards 565 nm with increasing  $\text{Er}^{3+}$  content. It was shown that annealing temperature of the ceramics leads to an increase emission intensity that correlate with improvement of crystal-line structure. The most intense up-conversion was observed in ceramics co-doped with 0.01 at. %  $\text{Er}^{3+}$  and 0.02 at. %  $\text{Yb}^{3+}$  after annealing at 1400 °C.

## References

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