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Structure and Up-Conversion Luminescence of Er^{3+}/Yb^{3+} Co-Doped Lanthanum Zirconate Ceramics

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$La_2Zr_2O_7$:Er, Yb nanoceramics have been obtained. Its structural and up-conversion luminescent properties were investigated. Under 980 nm laser excitation, the ceramics produced intense green and red up-conversion emission. The influence of Er^{3+} concentration and annealing conditions on the emission intensities has been discussed. The fabricated ceramics are expected to be an efficient up-conversion material with potential applications for laser diodes, display devices, detectors where the near infrared excitation is required.

Keywords: Ceramics; rare earths doping; up-conversion luminescence.

1. Introduction

Up-conversion luminescence (UCL) is an optical process involving the absorption of several excitation photons followed by the emission of a single photon with a shorter wavelength. It is a typical intrinsic property of materials co-doped with rare-earth ions, such as Er^{3+}, Tm^{3+}, Ho^{3+}, etc., which have a complex structure of electronic energy states and can produce visible emission under IR excitation. Such materials attract great interest due to broad application for phosphors in solid-state lightning, lasers, displays, solar cells, labels of biomolecules.[1–6]

Among well-known host matrices like single crystals, glass and glass ceramics, materials based on crystalline ceramics with pyrochlore/fluorite structure can be prospective. Pyrochlores have the general formula $A_2B_2O_7$, where A is a larger divalent or trivalent cation, in particular rare-earth elements like La^{3+}, Ce^{3+}, Gd^{3+}, while B is a smaller tetravalent cation, typically Ti, Zr, Hf, Sn.[7] In the pyrochlore structure, cation A is eight-coordinated and located within a distorted cubic coordination polyhedron, and cation B is six-coordinated and located in octahedral sites. The stability of these compounds is determined by the ratio of the radii of cations, r_A/r_B.[7]

Among the wide range of pyroclores, $La_2Zr_2O_7$ is employed in a variety of different applications, thanks to its attractive thermal, catalytic, optical, electrical and magnetic properties. In particular, this material has a huge potential of applications as a suitable phosphor matrix. Therefore, the current work is aimed at developing of optically active zirconate nanoceramics doped with rare-earth elements as perspective and efficient up-conversion material.

2. Experimental

The sol–gel approach was used for preparation of the experimental samples. This involves gel formation using $Ln(NO_3)_3 \cdot xH_2O$ (Ln = La, Er, Yb) and $ZrO(NO_3)_2 \cdot xH_2O$ from starting solutions. The prepared gel was dried, calcined at 800°C/4 h, ground and pressed into discs of about 1 mm thickness. The discs were annealed using the heating ramp of 10°C/min up to 1100–1500°C with the annealing time of 3 h.

The samples were labeled as 0.01; 0.02; 0.05; 0.10. The label corresponds to the Er^{3+} concentration (in at.% by La ions) at constant concentration of Yb at the level of 0.02 at.% by La ion. Density of the ceramics was in the range of 4.5–5.5 g/cm.

Phase identification of the products was carried out by X-ray diffraction (XRD) over the 2Θ range of 10–100° with CoKα radiation. The Williamson–Hall method was used for calculations of coherent scattering region (CSR) size and microstress values.

UCL spectra were recorded using a Fluorolog FL3-21 spectrometer (Horiba, France) equipped with PMT (R928) detector for visible and InGaS detector for NIR spectral range with 980 nm diode laser as an excitation source at the excitation power of 50 mW. KG5 filter was used to eliminate the second-order reflection from the spectrometer grating. All recorded spectra were subsequently corrected for the filter spectral profile. The standard CIE chromaticity coordinates were evaluated. In general, the color of any light source can be represented as an (x, y) coordinate in the color space.

3. Results and Discussion

The UCL spectra of the $La_2Zr_2O_7$:Er, Yb ceramics are shown in Fig. 1. The same emission lines were found for this series of the samples. Only the intensities in the green and red region were dependent on the composition and annealing temperature.

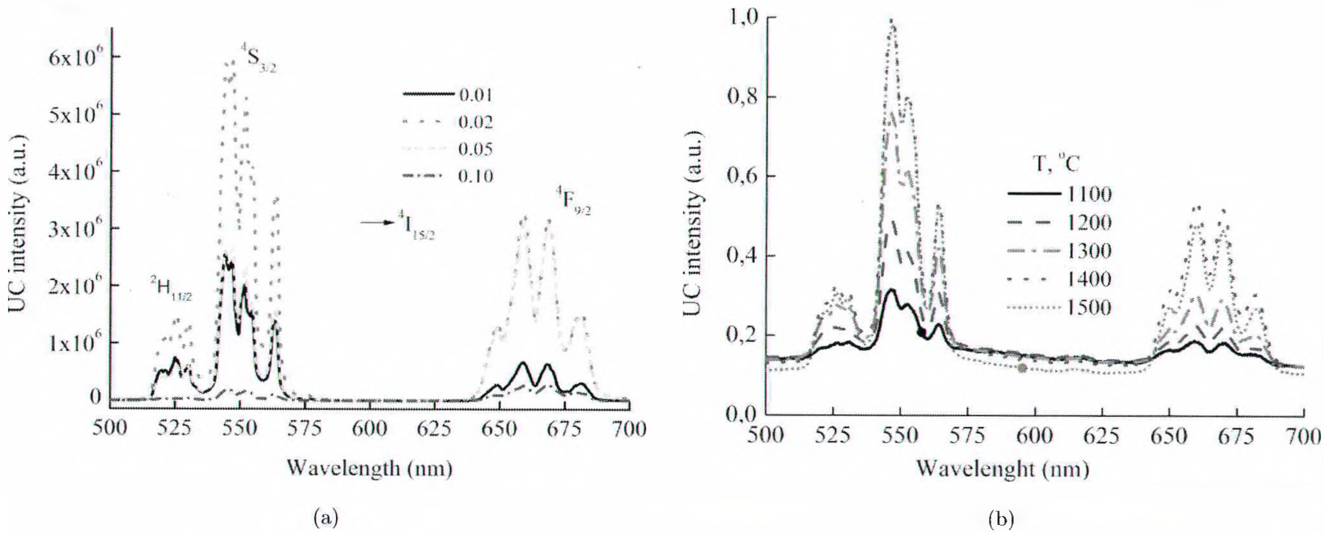

Fig. 1. UCL spectra (a) of $La_2Zr_2O_7$:Er,Yb ceramics annealed at 1400°C and evolution of UCL spectrum of $La_2Zr_2O_7:Er_{0.01}Yb_{0.02}$ with the annealing temperature (b). $\lambda_{ex} = 980$ nm.

The emission in the green region (500–550 nm) is related to the $^2H_{11/2}\rightarrow{}^4I_{15/2}$ (525 nm) and $^4S_{3/2}\rightarrow{}^4I_{15/2}$(545 nm) transition in Er^{3+} ions. The red emission in the 655–680 nm range is related to the $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transition in Er^{3+}.

The green UCL intensity shows nonmonotonic behavior depending on the concentration and reaches the maximum for the sample with 0.01 at.% of Er^{3+}, while the red UCL reaches the maximum intensity for the samples with 0.05 at.% and 0.1 at.% of Er^{3+}. An analysis of RGB color coordinates indicated that average emitted color induced by up-conversion changed in the range of green to yellow from ~ 550 nm towards 565 nm with increasing of Er^{3+} content. Temperature effect upon UCL can be attributed to a reduction of crystal lattice defects and decrease of ceramics porosity. XRD patterns (Fig. 2) were recorded for the $La_2Zr_2O_7$:$Er_{0.01}Yb_{0.02}$ ceramics obtained at 1100–1500°C.

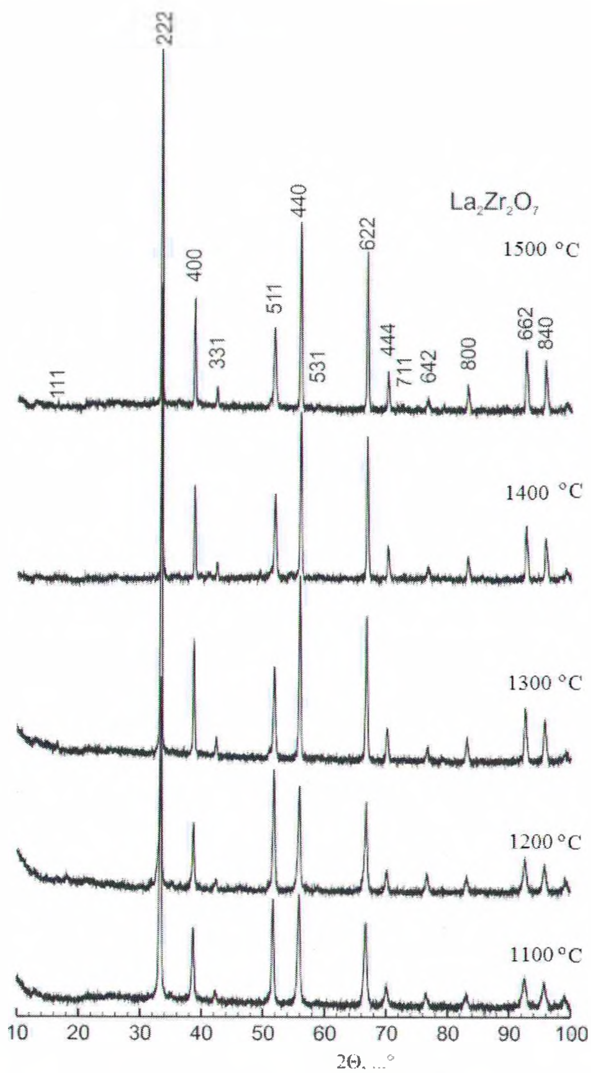

Fig. 2. XRD patterns of the $La_2Zr_2O_7$:$Er_{0.01}Yb_{0.02}$ ceramics obtained at different temperatures (indicated) indexed for $La_2Zr_2O_7$.

All reflections correspond to the $La_2Zr_2O_7$ phase (96-200-2249). 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 unit cell parameter for the investigated samples changes from 10.7855 Å to 10.7762 Å at increasing the annealing temperature from 1100°C to 1500°C. The calculated microstress values for the samples obtained at 1100°C and 1500°C are 9.53×10^{-6} and 7.9×10^{-6}, respectively. These data also indicate the crystalline structure improvement at rising annealing temperature due to the decrease of different kinds of defects. This is accompanied with increasing the emission intensity with annealing temperature [Fig. 1(b)]. The size of CSR for the investigated samples weakly depends on the annealing temperature being in the range of 70–75 nm.

4. Conclusion

The $La_2Zr_2O_7$:Er, Yb nanoceramics were synthesized using the sol–gel method and annealed at 1100–1500°C. Formation of the $La_2Zr_2O_7$ phase has been evidenced with XRD study. Effects of Er^{3+} concentrations and annealing temperature on UCL and structural properties of the ceramic materials were studied. It was shown that the annealing temperature of the ceramics leads to an increase of emission intensity that correlates with the improvement of crystalline structure. The most intense up-conversion was observed for the ceramics co-doped with 0.01 at.% Er^{3+} and 0.02 at.% Yb^{3+} after annealing at 1400°C.

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