Tm^{3+}, Li^{+} $ZnWO_4$: novel 2-μm laser crystal

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We report on the crystal growth, spectroscopic investigation, and laser performance of Tm^{3+}-doped monoclinic zinc tungstate (Tm:$ZnWO_4$). Tm^{3+}-doped $ZnWO_4$ crystals containing charge compensator (Li^+ ions) were grown using the Czochralski (Cz) method in air using a Pt crucible. The actual Tm^{3+} doping level for this second crystal was 1.59 at.% and the segregation coefficient is almost 0.4 owing to the positive effect of Li^+ codoping. Meanwhile, the actual Li^+ content in the crystal was measured to be 1.65 at.%, and the segregation coefficient is only ~ 0.2.

$ZnWO_4$ belongs to the monoclinic class adopting the C_{2h}^4 - P2/c space group and the 2/m point group, with a general multiplicity Z of 2. The lattice constants are a = 4.692Å, b = 5.721Å, c = 4.928Å, and the monoclinic angle β = a ^ c = 90.632°. $ZnWO_4$ optical properties are described within the optical indicatrix frame, featuring three mutually orthogonal principal axes denoted as N_p, N_m, and N_g. One of them (N_p) is parallel to the crystallographic ***b***-axis, aligned with the 2-fold symmetry axis. The other two axes of the optical indicatrix, N_m and N_g, lie in the ***a-c*** plane.

The polarized absorption spectra reveal a strong polarization anisotropy of absorption properties. The maximum absorption cross-sections σ_{abs} is 1.09×10^{-20} cm^2 at 803.6 nm and the corresponding absorption bandwidth is 16 nm for light polarization $\boldsymbol{E} \parallel N_g$. For the other two polarization states, σ_{abs} is smaller, amounting to 0.83×10^{-20} cm^2 at 807.7 nm (for $\boldsymbol{E} \parallel N_p$), and 0.24×10^{-20} cm^2 at 802.7 nm (for $\boldsymbol{E} \parallel N_m$).

A Judd-Ofelt analysis is conducted, the spontaneous emission probabilities, luminescence branching ratios and radiative lifetimes are determined. The crystal-field splitting of the $^3H_6$ and $^3F_4$ Tm^{3+} multiplets was achieved using low-temperature spectroscopy. The $ZnWO_4$ crystal exhibits a relatively large total Stark splitting of the Tm^{3+} ground state, $\Delta E(^3H_6)$ of 644 cm^{-1}, evidencing a relatively strong crystal-field for this material. This leads to the longest wavelength of a purely electronic transition $^3F_4 \rightarrow {}^3H_6$ of 2028 nm, i.e., above 2 μm, which is rarely observed for commonly used laser host crystals.

Polarized luminescence spectra and decay kinetic are obtained. Tm^{3+} ions in $ZnWO_4$ exhibit a significant polarization anisotropy of their emission properties that is favorable for achieving linearly polarized laser output. The maximum stimulated-emission (SE) cross-sections, σ_{SE} reaches 2.93×10^{-20} cm^2 at 1871 nm for light polarization $\boldsymbol{E} \parallel N_p$. In the long-wave spectral region where laser action is expected to be supported by the reabsorption from the ground-state for quasi-three-level 2-μm Tm lasers, the peak SE cross-sections are 0.77×10^{-20} cm^2 at 2015 nm and 0.70×10^{-20} cm^2 at 1971 nm also for light polarized $\boldsymbol{E} \parallel N_p$. Tm^{3+} ions exhibit smooth and broad emission spectral profiles extending beyond 2 μm, positioning Tm^{3+}-doped $ZnWO_4$ as a promising candidate for generation of femtosecond pulses in this spectral range which is well detuned from the structured absorption of water vapors in the air.

The decay of $^3F_4$ level is well described by the single-exponential law, yielding a luminescence lifetime τ_{lum} of 1.57 ms for the powdered sample, as compared to 2.08 ms for the bulk crystal.

The laser element was cut from the annealed crystal for light propagation along the N_g optical indicatrix axis (N_g-cut). The continuous-wave Tm^{3+}, Li^+: $ZnWO_4$ laser generated a maximum output power of 282 mW at 1964-1983 nm (exhibiting a broad laser spectrum) with a slope efficiency η of 14.7% with respect the absorbed power and a laser threshold of 188 mW. The combined attributes of large Stark splitting, polarized emission, spectral broadening, and prolonged luminescence lifetime position Tm-doped $ZnWO_4$ crystals as promising candidates for advanced laser systems.

This work has been supported by Russian Scientific Fund (grant №23-22-00416).