

On the potential of BaSO₄:Mn⁶⁺ for broadly tunable laser emission in the near infrared spectral region

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Because of the strong electron-phonon coupling of the emitting 3d orbitals in transition-metal (TM) ions, 3d systems exhibit luminescence with typically several hundred nm of spectral bandwidth. TM-ion-doped materials are, therefore, of high interest for applications as tunable and short-pulse lasers. Whereas many TM-ion-doped systems suffer from excited-state absorption (ESA), systems with a d¹ electron configuration possess only one excited 3d level and ESA into higher-lying 3d levels is impossible (however, ESA can occur owing to transitions into the conduction band and conduction-band-related energy levels).

Mn⁶⁺ is a promising ion for a tunable laser system, and near-infrared emission from Mn⁶⁺ was observed in several host lattices. In BaSO₄, the room-temperature stimulated-emission cross section is larger than the excited-state-absorption cross section in the spectral range 920-1600 nm [1], i.e., as a laser material BaSO₄:Mn⁶⁺ can offer a broad tuning range.

The fabrication of Mn⁶⁺-doped BaSO₄ layers requires a particular growth method at low temperatures, since the Mn⁶⁺ ions tend to reduce to Mn⁵⁺ at $T \geq 600^\circ\text{C}$. We have grown Mn⁶⁺-doped BaSO₄ layers at low temperatures using liquid-phase epitaxy (LPE). We used a CsCl-KCl-NaCl solvent for the LPE of BaSO₄:Mn⁶⁺ with a low solidification temperature of 480°C in order to keep the temperatures well below 600°C to prevent chemical reduction of Mn⁶⁺ to Mn⁵⁺. The nominal Mn⁶⁺ concentration was up to 1 mol% with respect to S⁶⁺. High quality layers with thickness of up to 580 μm, lack of large-size inclusions, and low defect concentration were achieved [2].

The Mn⁶⁺-doped BaSO₄ layers were investigated spectroscopically by absorption and emission measurements at room temperature (see Fig. 1) and the incorporation of manganese solely in its hexavalent oxidation state into our layers was confirmed [2]. The Mn⁶⁺ absorption bands are ²E → ²T₂ at 700-900 nm and a ligand-to-metal charge-transfer band at 500-650 nm. Excitation into these bands leads to broadband Mn⁶⁺ emission between 850 and 1600 nm. The fluorescence lifetime was measured to be 0.6 μs [2]. A relatively small reabsorption from the ground state is visible in the region of the fluorescence emission.

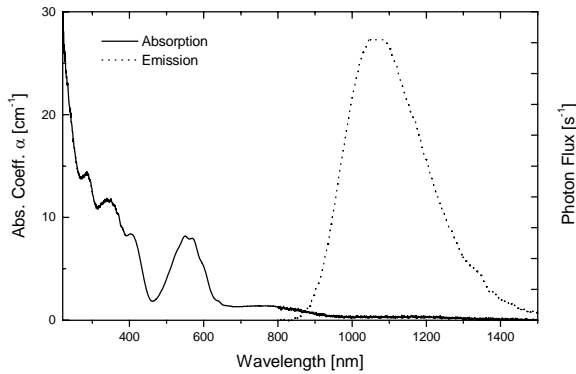


Fig. 1: Absorption and emission spectra of BaSO₄:Mn⁶⁺.

We find that pumping around 800 nm and providing high reflectivity of the cavity mirrors at 1150 nm cannot enable laser emission, because the ratio of ~5:1 between pump absorption cross-section and laser reabsorption cross-section is too small to allow for sufficient pump absorption and simultaneously avoid significant reabsorption of the oscillating laser light. In contrast, when pumping at 532 nm and providing high reflectivity at 1500 nm, this ratio becomes ~140:1. We conclude that laser oscillation of BaSO₄:Mn⁶⁺ at the longer wavelength side of the emission should be possible.

- [1] T.C. Brunold, H.U. Güdel, S. Kück, G. Huber, *J. Opt. Soc. Am. B* **14**, 2373 (1997).
- [2] D. Ehrentraut, M. Pollnau, S. Kück, *Appl. Phys. B* **75**, 59 (2002).

With the measured spectroscopic data, we performed a numerical simulation in order to investigate the future laser potential of BaSO₄:Mn⁶⁺. Since reabsorption from the ground state especially in the wings of the pump absorption may play a significant role in such a ground-state laser system, the rate equations for the excited-state population density and the photon density in the cavity were solved with longitudinal and radial resolution. The pump and laser wavelengths, dopant concentration, and length of the active medium were optimized with respect to a possible minimization of the laser threshold.