Flux growth and liquid-phase epitaxy of Mn^{6+}-doped molybdates and tungstates

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Transition-metal ions are suitable activators for tunable and short-pulse laser materials because of their broadband luminescence. Moreover, ions with a $3d^1$ electron configuration, such as Ti^{3+}, V^{4+}, Cr^{5+}, Mn^{6+}, are interesting with respect to laser application because they possess a simple energy level scheme. The presence of only two possible energy levels, ^2E and $^2T_2$, excludes an occurrence of undesirable exited-state absorption into higher 3d levels. Recently, the Mn^{6+} ion was investigated spectroscopically in different hosts. For instance, $BaSO_4$:Mn^{6+} exhibits broadband emission in the spectral region 850-1600 nm at room temperature and is a promising candidate as a near-IR tunable laser [1]. Suitable other candidates are molybdates and tungstates of Ca, Sr, and Ba. These well-known hosts of the scheelite ($CaWO_4$) family are chemically and mechanically stable, possess high thermal conductivity, and Mn^{6+} may substitute Mo^{6+}/W^{6+} in a well-defined tetrahedral oxo-coordination.

We performed a systematic investigation of Mn^{6+} in (Ca/Sr/Ba)(Mo/W)O_4 compounds which can be divided into three parts: (i) crystal-growth experiments in order to estimate the best conditions for (ii) liquid-phase epitaxy (LPE) of thin films doped with Mn^{6+}, (iii) whose spectroscopic properties are then studied. Since Mn^{6+} tends to be reduced to Mn^{5+} at temperatures T> 600°C, we used NaCl-KCl-CsCl as a solvent [2] for the flux and LPE experiments. Due to the low solidification temperature of the solvent (480°C), the maximum growth temperature could be kept below 600°C. The dependencies of the crystal dimensions versus solute concentration for all six (Ca/Sr/Ba)(Mo/W)O_4 compounds were constructed from the results of the flux experiments. Undoped (Ca/Sr/Ba)(Mo/W)O_4 substrates for further LPE experiments were then grown by the Czochralski technique. Because of the highest growth rates in the prelimenary flux experiments (tetrahedral bipyramides of up to 4×2×2 mm were obtained) $BaMoO_4$ was chosen among the six compounds for the first LPE experiments. $BaMoO_4$:Mn^{6+} layers were grown with velocities of approximately 12 μm h^{-1} at temperatures of 510-480°C and absorption spectra were recorded. It was seen that solute raw materials that form $BaMoO_4$ by a chemical reaction tend to reduce the oxidation state of the manganese ion to Mn^{4+} whereas a growth using $BaMoO_4$ powder as the solute material leads to crystals that incorporate Mn^{6+}. The growth of Mn^{6+}-doped layers for the other scheelite compounds and further spectroscopic investigations are currently in progress.

[1] D. Ehrentraut, M. Pollnau, S. Kück, Appl. Phys. B **75**, 59 (2002)
[2] D. Ehrentraut, M. Pollnau, J. Cryst. Growth **234**, 533 (2002)