

Flux growth and liquid phase epitaxy of undoped and Mn⁶⁺-doped sulfates, tungstates, and molybdates

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The Mn⁶⁺ ion is a promising activator ion for tunable and short-pulse laser materials because of its broadband luminescence in the spectral region 850-1600 nm and its simple 3d¹ electronic configuration, which excludes an occurrence of undesirable excited-state absorption into higher 3d levels. However, hexavalent manganese can be stabilized only in the tetrahedral oxo-coordination and easily reduces to Mn⁵⁺ or Mn⁴⁺ at temperatures above 600°C. Recently, flux [1] and liquid-phase epitaxy (LPE) [2] growth of Mn⁶⁺-doped sulfates has been reported, while except for BaMoO₄:Mn⁶⁺ [3] investigations on the mechanically more stable alkaline-earth-metal molybdates and tungstates as possible host materials for efficient Mn⁶⁺ incorporation have as yet not been reported.

We investigated the growth conditions of undoped and Mn⁶⁺-doped MAO₄, with M = Ca, Sr, Ba and A = S, Mo, W, from the ternary NaCl-KCl-CsCl solvent at temperatures 480-600°C. The growth rates increase in the series tungstates < molybdates < sulfates and depending on the cation, in the series Ca < Sr < Ba. The dopant ion Mn⁶⁺ can be easily incorporated into BaSO₄, less well into BaMoO₄ and BaWO₄, whereas for Ca- and Sr-containing tungstates and molybdates no significant doping was found, independent on the concentration of Mn⁶⁺ in the liquid solution. Moreover, reduction of the Mn⁶⁺ ion cannot be avoided, even at the presence of oxidizing additives such as K₂CO₃ or NaOH.

LPE was employed for growing Mn⁶⁺-doped layers of BaAO₄ compounds. Growth velocities of 3-5 μm/h in the temperature interval from 490-540°C from chloridic solution, containing 0.3-1mol% of K₂MnO₄ with respect to the solute, delivered dark-pink BaSO₄ and slightly green BaMoO₄ and BaWO₄ layers up to 200 μm in thickness. With respect to high Mn⁶⁺ doping levels, BaSO₄ is the most suitable host material and its further investigation under different initial concentrations of manganese is currently underway.

[1] T.C. Brunold, H.U. Güdel, Inorg. Chem. 36, 1946 (1997).

[2] D. Ehrentraut, M. Pollnau, Appl. Phys. B 75, 59 (2002).

[3] T.C. Brunold, H.U. Güdel, Chem. Phys. Lett. 249, 77 (1996).