The method for control Mn charge state in the $MgTiO_3$ red phosphors

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Objectives

Recently, magnesium titanates have become important for applications in solid state lighting [1]. Specifically, their activation with Mn^{4+} ions results in a red emission which can be excited by light of blue LED chip. However, the control of manganese charge state remains one of the major challenges of Mn doped compounds [1].

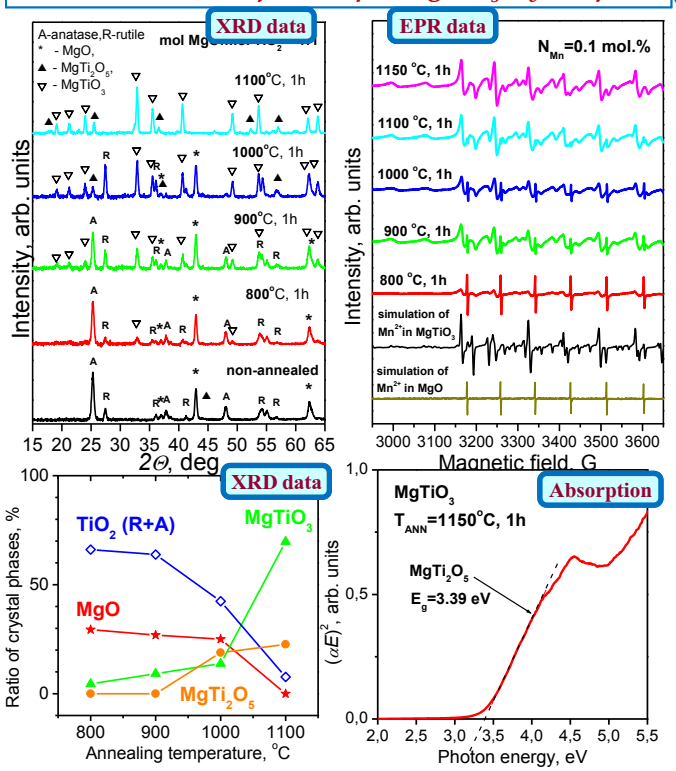
The **aim of the present work** was to study Mn incorporation in crystal lattice of $MgTiO_3$ fabricated through a solid-state reaction route and to develop the method for manipulating Mn charge state in the Mn-doped $MgTiO_3$ red phosphor.

Experimental details

The Mn-doped $MgTiO_3$ phosphor was produced via sintering in air at 800-1200°C for 1 or 3 h of a mixture of MgO and TiO_2 powders under different molar ratio. An aqueous solution of $MnSO_4$ was added to powder mixture to provide Mn content of 0.1 mol.%.

X-ray diffraction (XRD) study was carried out using X-ray diffractometer Philips X'Pert-MRD with the Cu$K\alpha_1$ radiation. **Electron paramagnetic resonance (EPR)** measurements were carried out using X-band EPR spectrometer Varian E12 (~ 9.5 GHz). The **photoluminescence (PL)** spectra were excited by a 409-nm diode laser and by the light of a Xe lamp passed through the grating monochromator. PL relaxation was recorded under pulse 410 nm laser excitation.

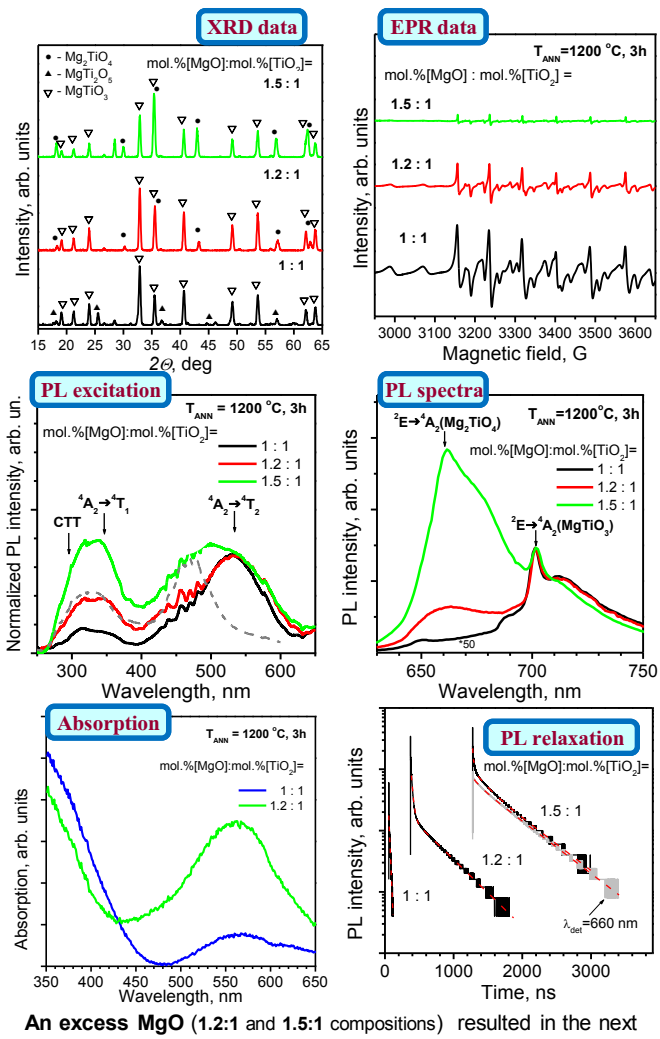
Results. Formation of Mn-doped $MgTiO_3$ crystal phase



XRD showed that $MgTiO_3$ phase formed starting from 800°C. The process is accompanied by formation of $MgTi_2O_5$ side phase following the reaction: $TiO_2 + MgTiO_3 = MgTi_2O_5$. The $MgTi_2O_5$ phase causes strong band-to-band absorption of UV light up to 380 nm.

The Mn-doped $MgTiO_3$ of stoichiometric composition (mol.%[MgO] : mol.%[TiO_2] = 1:1) showed weak absorption and weak red PL due Mn^{4+} ions. The PL decay curve showed single exponential behavior with relaxation time of ~17 μs. The EPR study revealed that at all annealing temperatures Mn incorporated in $MgTiO_3$ as Mn^{2+} mainly.

Results. The effect of excess MgO on crystal phase formation and charge state of Mn ions in $MgTiO_3$



An excess MgO (**1.2:1** and **1.5:1** compositions) resulted in the next changes in characteristics of Mn-doped $MgTiO_3$ phosphor:

- $MgTi_2O_5$ side phase disappeared, but Mg_2TiO_4 side phase emerged
- the PL band at ~701 nm due to Mn^{4+} ions in $MgTiO_3$ phase increased in intensity in ~50 times;
- the absorption due to Mn^{4+} ions in $MgTiO_3$ increased in intensity;
- red PL band at ~660 nm caused by Mn^{4+} in Mg_2TiO_4 emerged;
- the PL decay curve showed bi-exponential behavior with relaxation times of ~17 and 400 μs, the latter due to Mn^{4+} ions in Mg_2TiO_4;
- intensity of the EPR signal caused by Mn^{2+} ions decreased.

Conclusions

In $MgTiO_3$:Mn phosphor synthesized under stoichiometric composition, Mn incorporates as Mn^{2+} mainly. Low intensity of Mn^{4+} red PL is explained by its thermal quenching, partial absorption of UV excitation light by $MgTi_2O_5$ side phase and low concentration of Mn^{4+} centers.

An excess MgO causes strong increase of Mn^{4+} ion concentration and the decrease of Mn^{2+} ion concentration, and affects formation of $MgTi_2O_5$ and Mg_2TiO_4 side phases. This **results in up to 50 times increased Mn^{4+} red PL**. It is concluded that excess MgO can be used for control of Mn charge state in magnesium titanates.

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References [1] L. Borkovska, et.al., // J. Mater. Sci.: Mater. Electron. 31 (2020) 7555.