Sol-gel derived $ZnAl_2O_4$ nanopowders co-doped with Cr^{3+}, Er^{3+} and Yb^{3+} ions

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Motivation

Zink aluminate $ZnAl_2O_4$ with the spinel structure is well known multifunctional material widely used as ceramics, sensors, catalysts and optical host materials due to high chemical and thermal stability, high quantum yield and large surface area. It is known that co-doping spinel by Er^{3+} or Er^{3+}/Yb^{3+} ions lead to increasing time of long lasting NIR luminescence and upconversion emission intensity in those spinels.

Synthesis

Low-temperature citrate sol-gel method was used for the synthesis of nanocrystalline phosphors of nominal composition $ZnAl_{1.994-x}O_4:Cr_{0.003}Er_{0.003}Yb_x$ (x = 0.009, 0.015 and 0.021). In contrast to the traditional high-temperature solid-state synthesis, the applied method allowed to obtain phase-pure nanopowders of all three series of materials with Cr^{3+}:Er^{3+}:Yb^{3+} ratios of 1:1:3, 1:1:5 and 1:1:7 at a minimal heat treatment temperature of 700 °C.

Results

The average grain size of as-obtained spinel-type materials derived from X-ray diffraction data increases from ~33 nm after initial crystallization at 700 °C up to 73-75 nm in the materials heat-treated at 1200 °C. Spot-check investigation of sample morphology by scanning electron microscopy revealed a platelet-like structure with plates formed by dense packed near spherical grains of 50-150 nm diameter.

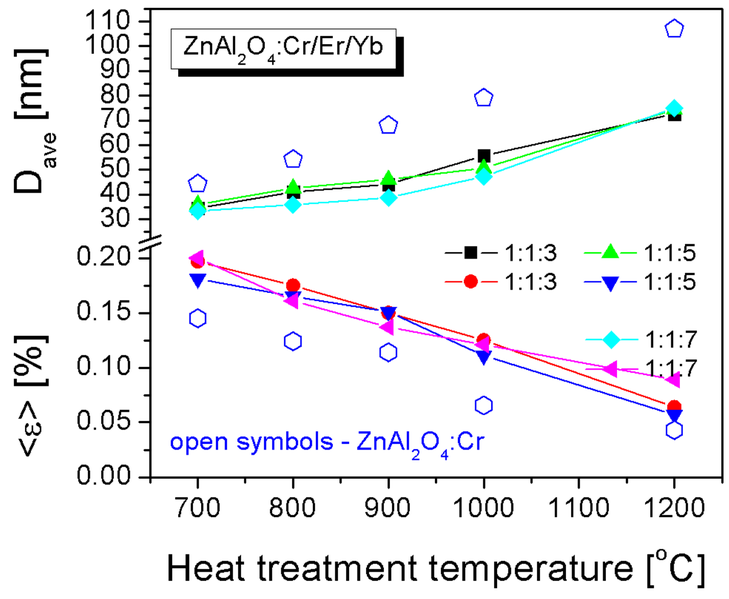
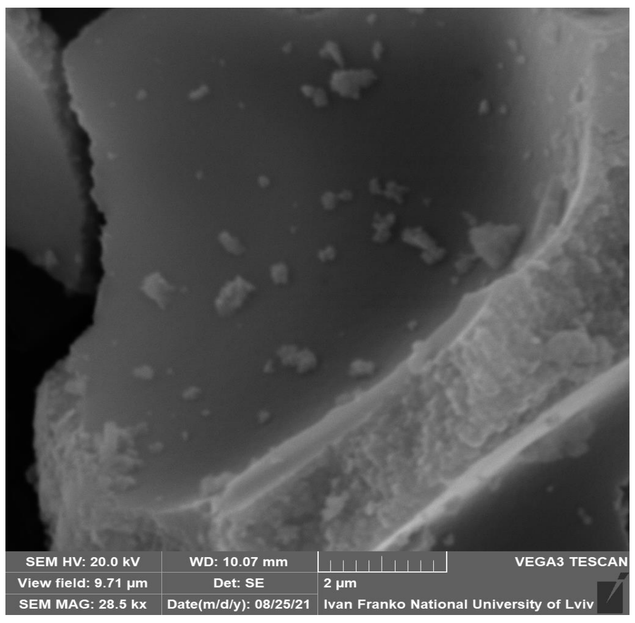


Fig.1 Average grain size $<D_{ave}>$ and microstrains $<\varepsilon>$ of $ZnAl_2O_4$:Cr/Er/Yb series *vs* heat treatment temperature



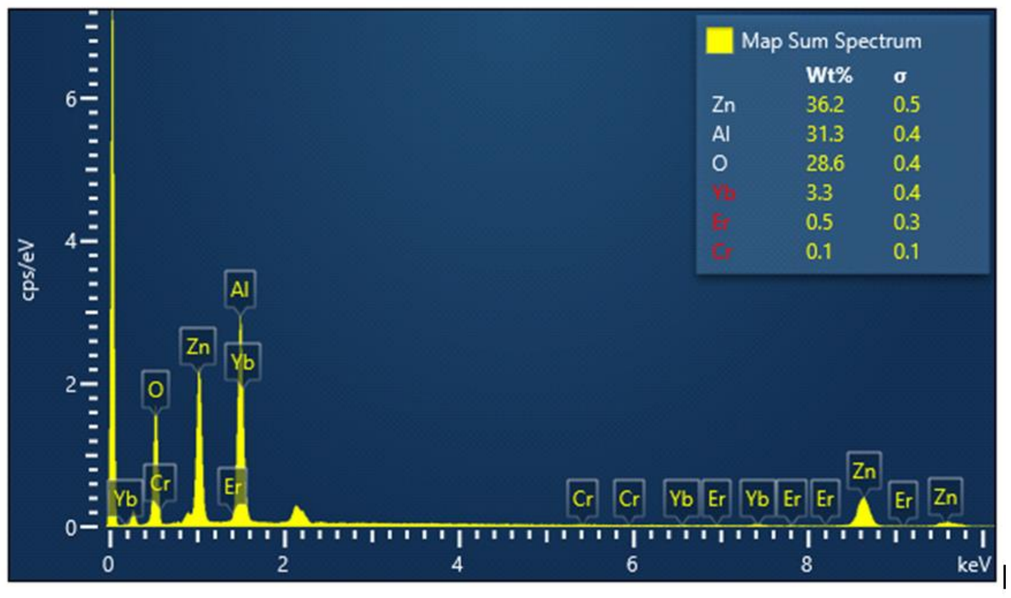


Fig. 2 SEM image and EDX map of the $ZnAl_{1.994-x}O_4:Cr_{0.003}Er_{0.003}Yb_x$ (x = 0.021), annealed at 1200 C

The unit cell dimensions of triply doped $ZnAl_2O_4$:Cr,Er,Yb materials are systematically higher than those for RE-free $ZnAl_2O_4$:Cr samples, thus proving effective incorporation of the large Er^{3+} and Yb^{3+} ions into $ZnAl_2O_4$ lattice. Reduction the unit cell with increasing threat treatment can be explained (i) by limited solubility of RE ions in $ZnAl_2O_4$ crystal matrices and/or (ii) by partial redistribution (inversion) of Al and Zn cations in the tetrahedral and octahedral positions of spinel structure.

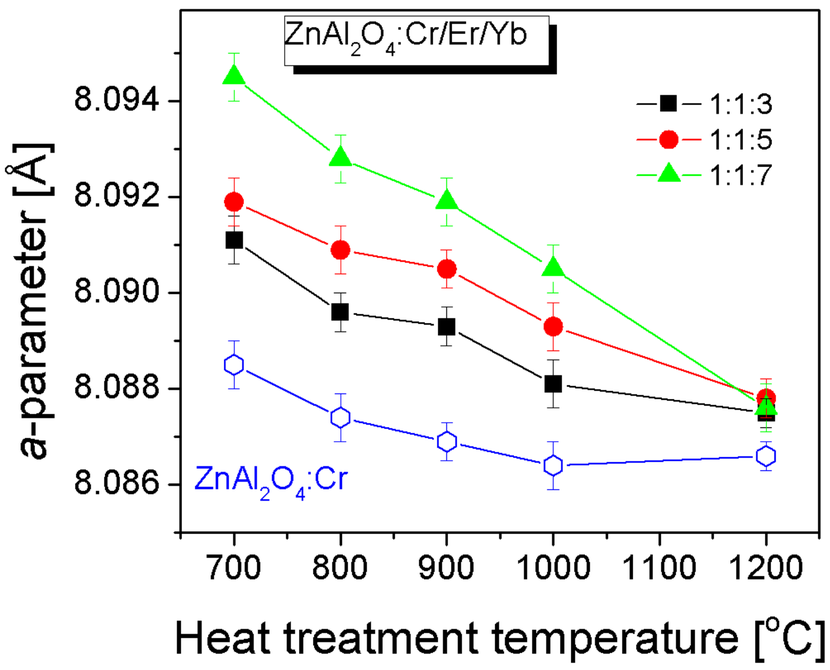
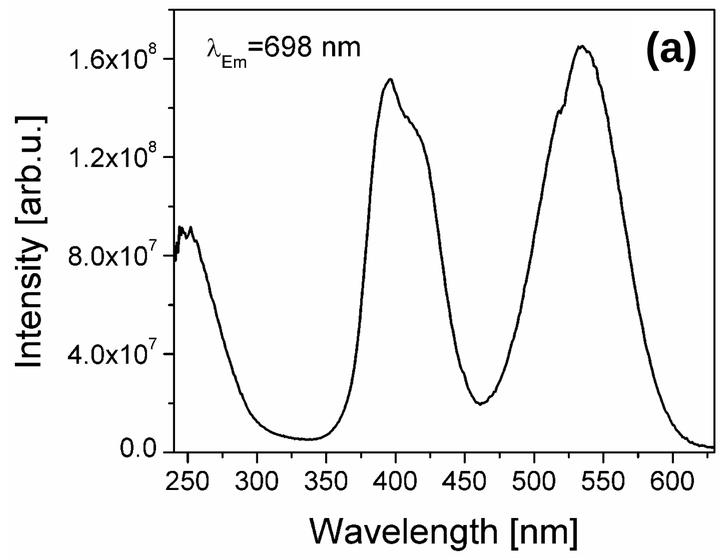


Fig.3 Dependencies of unit cell parameter of triply doped ZAO:Cr,Er,Yb on heat treatment temperature



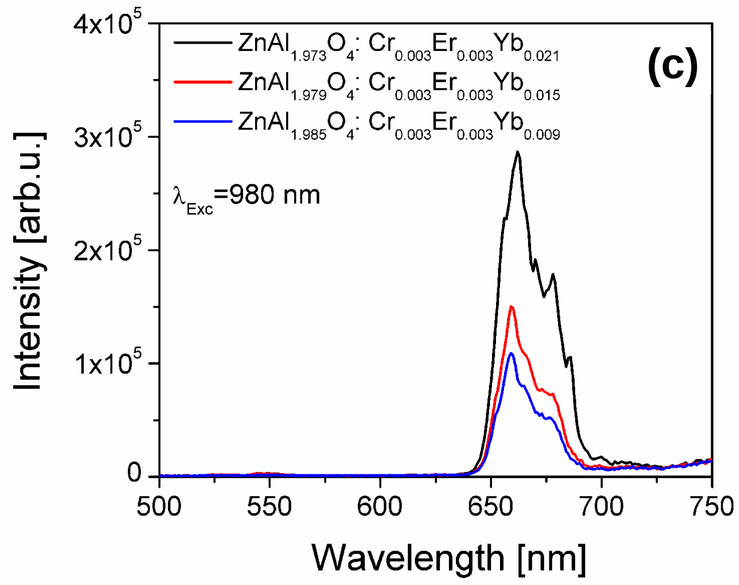


Fig. 4 The excitation (a), emission (b) and upconversion (c) spectra of triply doped $ZnAl_2O_4$:Cr,Er,Yb, annealed at 1200 °C

The excitation spectra of the $ZnAl_2O_4$:Cr:Er:Yb phosphors consist of three wide bands, which correspond to the $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4T_2$ transitions in Cr^{3+} ions in octahedral sites. The wide emission band of upconversion spectra correspond only to Er^{3+} ions. Luminescence of Cr^{3+} ions at excitation 980 nm are absent.

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