Radiation Measurements 90 (2016) 47–50

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Luminescence spectroscopy of Eu^{3+} and Mn^{2+} ions in $MgGa_2O_4$ spinel

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HIGHLIGHTS

- Host luminescence is presented by a broad band with a maximum at 430 nm and has a complex nature.
- Charge transfer bands from lattice to Mn^{2+} and Eu^{3+} ions were found around 260 and 280 nm, respectively.
- Activator luminescence intensity reaches the maximum at 4 mol.% of Eu^{3+} ions concentration.

ARTICLE INFO

Article history:
Received 23 October 2015
Received in revised form
26 November 2015
Accepted 3 December 2015
Available online 10 December 2015

Keywords:
Magnesium gallate $MgGa_2O_4$
Rare-earth ions Eu^{3+}
Transition metals Mn^{2+}
Co-doping
Matrix luminescence
Photoluminescence and excitation spectra

ABSTRACT

Photoluminescence and excitation spectra of the spinel-type $MgGa_2O_4$ with 0.5 mol. % Mn^{2+} ions and Eu^{3+} content from 0 to 8 mol. % have been investigated in this work at room temperature. Polycrystalline samples were synthesized via high-temperature solid-state reaction method. Photoluminescence spectra of all samples exhibit host emission presented by a broad "blue" band peaking ~430 nm, which consists of at least three elementary bands that correspond to different host defects. Excitation of the host luminescence showed the broad band with a maximum at 360 nm. Characteristic bands of d–d transitions of Mn^{2+} ions and f–f transitions of Eu^{3+} ions together with charge-transfer bands (CTB) of these ions were also found on the excitation spectra. Mn^{2+} and Eu^{3+} co-doped samples emit in green and red spectral regions. Mn^{2+} ions are responsible for the green emission band at 505 nm ($^4T_1 \rightarrow {}^6A_1$ transition). The studies of photoluminescence spectra of activated samples with different Eu^{3+} ions content show characteristic f–f luminesecence of Eu^{3+} ions. The maximum of Eu^{3+} emission was found at 618 nm ($^5D_0 \rightarrow {}^7F_2$) and optimal concentration of activator ions was around 4 mol. %.

1. Introduction

$MgGa_2O_4$ and $ZnGa_2O_4$ spinels have attracted great attention of researches due to their dielectric and optical properties, radiation resistance and high temperature stability. Spinel crystals and ceramics doped with rare-earth ions are promising materials in solid-state laser, thin film electroluminescence displays (TFELD), field emission displays (FED) and vacuum fluorescent displays (VFD) (Y. Zhang et al., 2014). In particular, magnesium gallate doped with Eu^{3+} ions has excellent luminescent properties in "red" and "orange" spectral region (e.g. Ya. Li et al., 2009). Moreover, those spinel compounds doped with transition metals could be used for fiber optic thermometry (V. T. Gritsyna et al., 2006).

The prevailing number of researchers associate the matrix luminescence with host defects, in particular, oxygen vacancies. All pure spinel compounds have the host luminescence in "blue" spectral region. The presence of luminescence of lattice defects in magnesium gallate spinel was reported in the research of (Zh. Lui et al., 2009). A broad luminescence band peaking around 460 nm has been found in these studies. The authors (S. S. Yi at al., 2002) have studied the host luminescence of $ZnGa_2O_4$ films grown at different oxygen pressure and obtained similar results. Also, here were detected three overlapping emission bands at 420, 465 and 520 nm. Nevertheless, the mechanism of the "blue" host emission is not established.

This paper reports about photoluminescence studies of $MgGa_2O_4$ co-doped with Mn^{2+} ions and different content of Eu^{3+} ions. Meanwhile, no phosphors with Eu^{3+} and Mn^{2+} co-doping were reported. The emission mechanisms of samples synthesized by solid state reaction method were also investigated.

2. Experimental details

Polycrystalline samples of $MgGa_2O_4$ with Eu^{3+} content from

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http://dx.doi.org/10.1016/j.radmeas.2015.12.003
1350-4487/

0 (nominal pure) to 8 mol. %, were prepared by high-temperature solid state reaction method. Magnesium oxide (MgO), β-gallium oxide (β-Ga_2O_3), europium (III) oxide (Eu_2O_3) and manganese oxide (MnO) were used as the starting materials. All reagents were at least 4N grade of purity. Powders of stoichiometric composition with 0, 2, 4, 6, 8 mol. % of Eu_2O_3 and 0.05 mol.% of MnO were ground in agate mortar for 6 h with further pressing in steel mold under the pressure of 150 kg/cm^2. Obtained tablets were annealed at 1473 K for 8 h in air. These samples were 4 mm in diameter and 1 mm thick.

XRD analysis were performed on STOE STADI P diffractometer with linear position-sensitive PSD detector using X-ray tube with Cu anode ($K\alpha_1$-radiation, $\lambda = 1.5406$ Å). The sensitivity range of detector is 5.5–7° 2Θ with a minimal step of 0.005°. Analysis of diffraction peaks was realized with STOE WinXPOW software package.

Photoluminescence measurements were carried out on spectrofluorometer CM2203 in 220–820 mn spectral range. All excitation and luminescence spectra were obtained with a spectral resolution of 1 nm. Excitation of luminescence was performed with 150 W xenon lamp. A Hamamatsu R928 photomultiplier was used as luminescence detector.

3. Results and discussions

X-ray diffraction measurements were performed on all investigated samples. The XRD patterns were compared with standard Powder diffraction data file ICSD data base No.37359. All investigated samples are spinel type structure compound with Fd3m space group (No. 227) with coordination number z = 8. No additional phases were detected. The XRD pattern of $MgGa_2O_4$: 4 mol.% Eu^{3+}, 0.05 mol.% Mn^{2+} samples is shown on Fig. 1. The average cell parameter of $MgGa_2O_4$: 4 mol.% Eu^{3+} 0.05 mol.% Mn^{2+} samples was determined: a = 8,27333(8) Å.

Excitation spectra of pure magnesium gallate spinel monitored at 430 nm (Fig. 2) shows a broad band peaking around 360 nm, which is associated with excitation of defect levels of the matrix inside the band-gap. In the spectral region 230–320 nm weak excitation with two small maximums approximately at 260 and 280 nm is observed. The excitation spectra monitored at the long-wavelength side of the host luminescence band (500 nm) shows a weak broad band in the spectral region 340–450 nm.

The excitation spectra of co-doped samples (Fig. 3) monitored at 430 show an additional band in near UV region peaking around

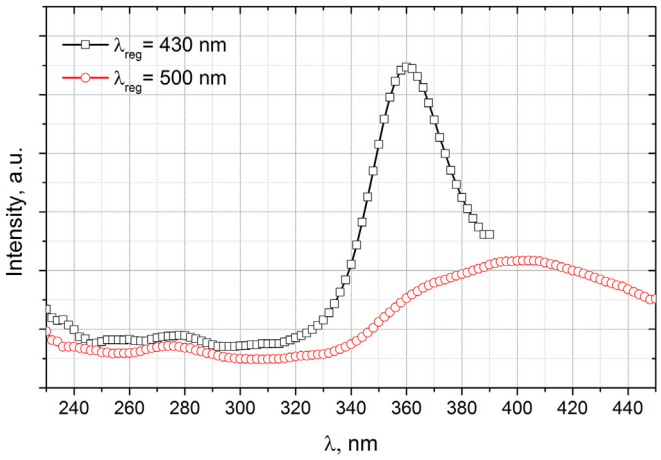

Fig. 2. Photoluminescence excitation spectra of pure magnesium gallate sample monitored at 430 nm (black line) and 500 nm (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

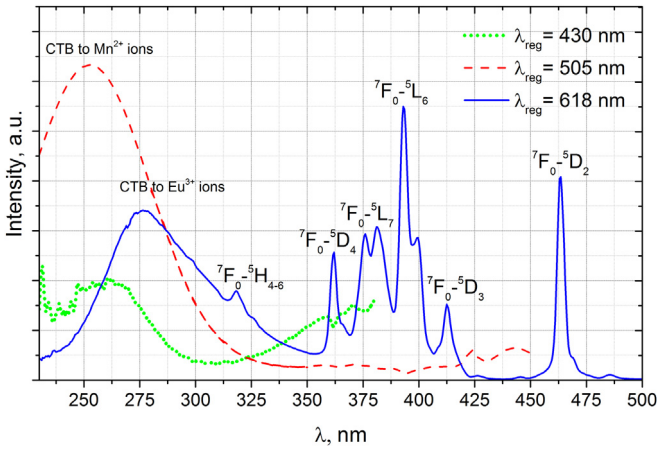

Fig. 3. Photoluminescence excitation spectra of $MgGa_2O_4$: 4 mol.% Eu^{3+}, 0.05 mol.% Mn^{2+} sample monitored at 430 nm (green line), 505 nm (red line) and 618 nm (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

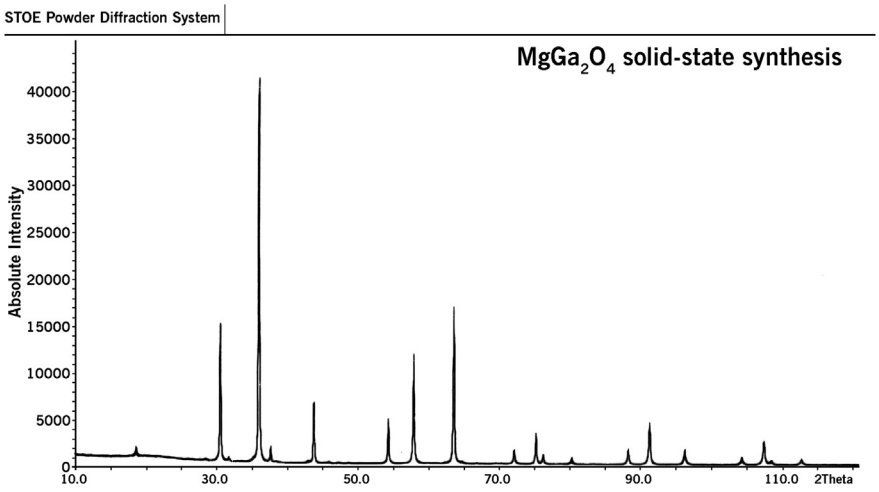

Fig. 1. XRD pattern of $MgGa_2O_4$: 4 mol.% Eu^{3+}, 0.05 mol.% Mn^{2+} samples.