



Novel visible phosphors based on MgGa_2O_4 - ZnGa_2O_4 solid solutions with spinel structure co-doped with Mn^{2+} and Eu^{3+} ions



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ABSTRACT

Photoluminescence excitation and emission spectra of $\text{Mg}_{1-x}\text{Zn}_x\text{Ga}_2\text{O}_4$ solid solutions ($x = 0; 0.25; 0.5; 0.75; 1.0$) co-doped with 0.05 mol% Mn^{2+} and 4 mol% Eu^{3+} ions have been investigated at room temperature. Polycrystalline samples were synthesized using high-temperature solid-state reaction technique. XRD measurements confirmed that all ceramic samples are compounds of a spinel structure. Lattice parameter follows linear dependence on composition that confirms Vegard's law for a $\text{Mg}_{1-x}\text{Zn}_x\text{Ga}_2\text{O}_4$ solid solution system. Complex broad luminescence band ranging from 350 to 475 nm ascribed to emission from host defects was found at the excitation in "band-to-band" spectral region. Noticeable intense matrix luminescence in ceramic samples with $x = 0.25$ and 0.5 was observed. Emission of Mn^{2+} ions is presented by an intense band with a maximum around 505 nm and shifts at different compositions. Intense excitation of Mn^{2+} ions was found around the fundamental absorption edge. Complex excitation nature of Mn^{2+} ions was suggested. The charge transfer band and $f-f$ excitation lines were found in excitation spectra of Eu^{3+} ions. Luminescence of Eu^{3+} ions is represented by a number of sharp $f-f$ lines in the 575–650 nm spectral region. Composition changing from MgGa_2O_4 to ZnGa_2O_4 leads to suppression of Eu^{3+} ions emission which shows a maximum at $x = 0.25$. Maximum of matrix luminescence and emission of Mn^{2+} ions were found at $x = 0.50$. Further increase of zinc amount in $\text{Mg}_{1-x}\text{Zn}_x\text{Ga}_2\text{O}_4$ solid solution leads to suppression of intensity of all luminescence bands. The influence of excitation wavelength and composition on the visible range luminescence intensity has been shown. Commission Internationale de l'Eclairage chromaticity diagrams are presented for different compositions and excitation conditions.

1. Introduction

Even though the complex oxide-based phosphors have been widely investigated, so far it didn't lose attention of a high number of researchers though the world. Among many oxide compounds, MgGa_2O_4 and ZnGa_2O_4 phosphors have attracted much attention due to great demand for new types of oxide semiconductors with high luminescence output [1–3]. These gallate spinel compounds have various potential applications in high performance displays, plasma display panels, field emission displays, electroluminescent displays and quick response cathode ray tubes that are still highly required [4]. MgGa_2O_4 and ZnGa_2O_4 exhibit a few potential advantages, in particular, of the superior chemical and thermal stability as well as electron beam bombardment tolerance with respect to sulfide phosphors that are the basic materials used in applications mentioned above [5].

Through increasing energy expenditures of civilization, a high number of scientists are searching for new methods of power saving. White-light emitting diodes (W-LEDs) are a high spot among sources of

white light. W-LED is a promising solid-state light approach due to their fascinating advantages of energy savings, high efficiency, longer lifetime and environmental safeness in comparison to conventional incandescent and fluorescent lamps [5,6]. Possible white lighting application could also be based on semiconductor properties of zinc and magnesium gallate spinel compounds. It gives a possibility to excite emission with electric field applied directly to the samples with no need of UV excitation [6].

Spinel compounds have attracted much attention, even though solid solutions of these compounds still aren't investigated, only a few papers were dedicated to this kind of studies. Tsai et al. reported about $\text{Mg}_x\text{Zn}_{1-x}\text{Ga}_2\text{O}_4$ compounds doped with Eu^{3+} ions synthesized via sol-gel technique [2]. There was shown that Eu^{3+} excitation lines become more prominent with increasing of Mg content. Interesting results were presented in the paper [7] that reports about luminescence properties of $\text{MgIn}_{2-x}\text{Ga}_x\text{O}_4$ solid solutions activated with Eu^{3+} ions. The main result of this paper is that no charge transfer band between activator ions and lattice was found. Samples with $x = 0.2$ show most intense

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luminescence of activator ions. Another remarkable investigation of the spinel solid solution was carried out by Moon et al. [8]. This paper reports about luminescence studies of MgGa_2O_4 together with $\text{MgGa}_{2-y}\text{Al}_y\text{O}_4$ ($y = 0.5 \div 2.0$) doped with Mn^{2+} ions. Partial substitution of Ga^{3+} to Al^{3+} cations leads to red-shift of the Mn^{2+} luminescence band. Such substitution also affects a luminescence intensity, which rises with increasing of Al^{3+} ions and reaches maximum at $y = 1.0$.

For the first time, properties of co-doped with Mn^{2+} and Eu^{3+} ions MgGa_2O_4 spinel compound were reported by Luchechko et al. [9,10]. These studies showed that co-doping affects relative intensities of matrix luminescence in “blue”, emission of Mn^{2+} in “green” and sharp luminescence lines of Eu^{3+} ions in “red” spectral regions. The optimal concentration of Eu^{3+} activator ions was identified around 4 mol% in MgGa_2O_4 : Mn, Eu samples.

This paper reports about photoluminescence investigations of $\text{Mg}_{1-x}\text{Zn}_x\text{Ga}_2\text{O}_4$ ($x = 0; 0.25; 0.50; 0.75; 1.0$) solid solutions co-doped with 0.05 mol% Mn^{2+} and 4 mol% Eu^{3+} ions synthesized using solid-state reaction method for various phosphor applications. The emission mechanisms of $\text{Mg}_{1-x}\text{Zn}_x\text{Ga}_2\text{O}_4$: Mn^{2+} , Eu^{3+} samples are proposed. Meanwhile, there are just a few reports about luminescence of solid solutions with the spinel structure and no papers on Mn^{2+} and Eu^{3+} co-doped MgGa_2O_4 - ZnGa_2O_4 solid solutions were found.

2. Experimental details

Polycrystalline samples of $\text{Mg}_{1-x}\text{Zn}_x\text{Ga}_2\text{O}_4$: Mn, Eu ($x = 0; 0.25; 0.50; 0.75; 1.0$) were prepared by high-temperature solid-state reaction method. Magnesium oxide (MgO), zinc oxide (ZnO), β -gallium oxide ($\beta\text{-Ga}_2\text{O}_3$), europium (III) oxide (Eu_2O_3) and manganese oxide (MnO) were used as initial materials. All reagents were at least 4N grade of purity. Powders of stoichiometric composition with 4 mol% of Eu_2O_3 and 0.05 mol% of MnO were ground in an agate mortar for 6 h with further pressing in a steel mold under the pressure of 150 kg/cm². Obtained tablets were annealed at 1200 °C for 8 hours in the air. These samples were 4 mm in diameter and 1 mm thick.

X-ray diffraction measurements were carried out in “Interfaculty scientific-educational laboratory of X-ray structure analysis” of Ivan Franko National University of Lviv. XRD analysis was performed on STOE STADI P diffractometer with linear position-sensitive PSD detector using X-ray tube with Cu anode ($\text{K}\alpha_1$ -radiation, $\lambda = 1.5406 \text{ \AA}$). XRD measurements were performed with 0.005° scanning step. Analysis of diffraction peaks was realized with STOE WinXPOW software package.

Photoluminescence measurements were carried out on spectrofluorometer CM2203 in the 220–820 nm spectral range at room temperature. All excitation and luminescence spectra were obtained with a spectral resolution of 0.5 nm. Excitation of luminescence was performed with 150 W xenon lamp. A Hamamatsu R928 photomultiplier was used as luminescence detector. All photoluminescence and excitation spectra were automatically corrected to the photomultiplier sensitivity and lamp intensity, respectively.

3. Results and discussions

X-ray diffraction measurements were performed for all investigated $\text{Mg}_{1-x}\text{Zn}_x\text{Ga}_2\text{O}_4$ ($x = 0; 0.25; 0.5; 0.75; 1.0$) solid solution samples co-doped with Mn^{2+} and Eu^{3+} ions. The XRD patterns were compared with standard powder diffraction data file ICSD No. 37359. All investigated samples are compounds of spinel structure with $Fd3m$ space group (No. 227). The typical XRD patterns of $\text{Mg}_{1-x}\text{Zn}_x\text{Ga}_2\text{O}_4$: Mn^{2+} , Eu^{3+} ($x = 0; 0.5; 1.0$) samples are shown on Fig. 1. Average cell parameters of MgGa_2O_4 , $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Ga}_2\text{O}_4$ and ZnGa_2O_4 samples co-doped with Mn^{2+} and Eu^{3+} ions were determined and are equal 8.2675 Å, 8.3069 Å, 8.3408 Å, respectively. An additional diffraction line is observed around 32.275° due to presence of $\beta\text{-Ga}_2\text{O}_3$ phase from 1% to 3%. The additional phase can appear as a result of evaporation of

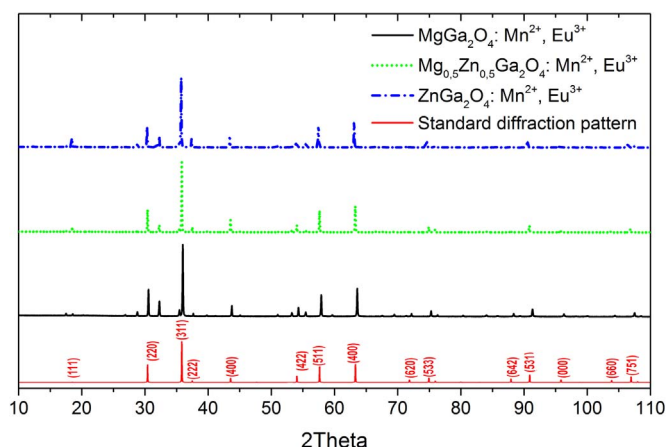


Fig. 1. XRD pattern of MgGa_2O_4 , $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Ga}_2\text{O}_4$, ZnGa_2O_4 samples co-doped with Mn^{2+} and Eu^{3+} ions synthesized via high-temperature solid state reaction method at 1200 °C and Standard diffraction pattern ICSD № 37359.

starting materials during annealing. It should be noted that Eu^{3+} doped spinels show a higher value of cell parameter with respect to pure MgGa_2O_4 and ZnGa_2O_4 [1,11]. It is known that Mn^{2+} and Eu^{3+} ions occupy tetrahedral (T_d point symmetry) and octahedral (O_h point symmetry) sites, respectively [2,12]. Thus, it can be explained by distortion of spinel lattice due to ionic radius mismatch of activator ions (0.66 Å for Mn^{2+} , 0.95 Å for Eu^{3+}) and host atoms (0.66, 0.74 Å, 0.62 Å for Mg^{2+} , Zn^{2+} , Ga^{3+}), respectively [4,5,13].

Lattice parameter depends on solid solution composition, usually it follows the Vegard's law. It is evidently seen that lattice parameter increases with changing of composition from magnesium to zinc gallate spinel compound. Obtained data for magnesium gallate (MgGa_2O_4) and zinc gallate (ZnGa_2O_4) solid solutions is depicted in Fig. 2. Linear dependence of lattice parameter on composition has been confirmed.

Photoluminescence excitation spectra of $\text{Mg}_{1-x}\text{Zn}_x\text{Ga}_2\text{O}_4$: Mn^{2+} , Eu^{3+} ($x = 0; 0.25; 0.50; 0.75; 1.0$) solid solutions at 430, 505 and 617 nm registrations are shown on Fig. 3. A broad excitation band in the 230–270 nm spectral region with a maximum around 235 nm was found at 430 nm registration for all samples Fig. 3(a). This band is in fundamental absorption spectral range and corresponds to the excitation of matrix luminescence. Matrix excitation band of $x = 0.25$ and 0.50 samples shows relatively strong intensity. The excitation spectra of $x = 0, 0.75$ and 1.0 samples were smoothed and 10 times increased due to low signal with respect to $x = 0.25$ and 0.50 samples. Together with that, a weak broad excitation band in the 300–360 nm spectral region was found in excitation spectra of $\text{Mg}_{1-x}\text{Zn}_x\text{Ga}_2\text{O}_4$: Mn^{2+} , Eu^{3+}

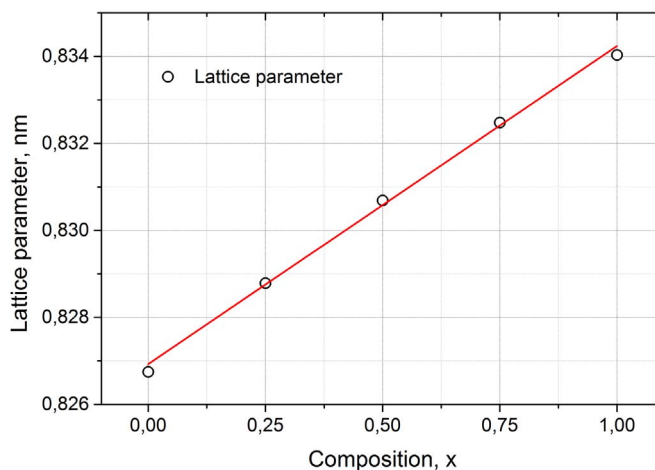


Fig. 2. Variation of lattice parameter for different composition of $\text{Mg}_{1-x}\text{Zn}_x\text{Ga}_2\text{O}_4$: Mn, Eu solid solutions. The solid line represents the Vegard's law.

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