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TL and OSL properties of Mn^{2+}-doped $MgGa_2O_4$ phosphor

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The oxide $MgGa_2O_4$ spinel ceramics doped with Mn^{2+} ions was synthesized by a solid-state reaction at 1200 °C in air. The activator concentration was equal 0.05 mol% of MnO. Phase purity of the synthesized samples was analyzed by X-ray diffraction technique. This spinel ceramics show efficient green emission in the range from 470 to 550 nm with a maximum at about 505 nm under UV or X-ray excitations, which is due to Mn^{2+} ions. $MgGa_2O_4$: Mn^{2+} exhibits intense thermoluminescence (TL) and optically stimulated luminescence (OSL) after influence of ionizing radiation. Are complex nature of the TL glow curves is associated with a significant number of structural defects that are responsible for the formation of shallow and deep electron traps. In this work, time-resolved OSL characteristics of the samples exposed to beta particles are reported for the first time. A light from green LED was used for optical stimulation. Obtained TL and OSL results suggest $MgGa_2O_4$:Mn^{2+} as perspective material for further research and possible application in radiation dosimetry.

1. Introduction

It is known that oxide materials with spinel structure attract great attention due to their perfect optical and luminescent properties, good radiation damage resistance, high-temperature and chemical stability. In particular, magnesium aluminate ($MgAl_2O_4$) and gallate ($MgGa_2O_4$) compounds are promising materials as a host for light emitting diodes (LEDs), solid-state lasers and different kinds of display technologies as well as phosphors for various luminescent applications [1–4].

In recent years, a great interest has been focused on luminescence properties of a wide of oxide-based phosphors in order to obtain efficient luminescent materials in the green spectral region. Mn^{2+}-doped luminescent materials have been known to show a wide-ranging emission from 480 to 650 nm depending on the crystal field of the host material [5,6]. The photoluminescence of such materials is caused by the transitions of 3 d^5 electrons of the manganese ion acting as an activating center. In particular, Mn^{2+}-activated $MgGa_2O_4$ phosphor exhibits long-lasting phosphorescence which has application in optical storage media and flat display devices [5].

In the last decades, optically stimulated luminescence (OSL) has become of high interest as the readout technique applicable in radiation dosimetry that is an alternative to thermoluminescence (TL). The requirement of available and durable dosimetry devices stimulates researchers to search and explore new materials for thermoluminescence and especially OSL dosimetry [7,8]. The intensity of the OSL signal is dependent on the radiation dose and can be used as a basis for a passive integrating dosimetry method.

It should be noted, that time-resolved OSL (TR-OSL) method, which uses a pulsed stimulation, has several advantages over the continuous wave OSL (CW-OSL), especially a very high signal to background ratio because the background measured after the pulse is due to the only dark current of a photomultiplier tube (PMT) [9,10]. TR-OSL decay curve (also called the TR-OSL spectrum) enables one to obtain information about the recombination processes. In such a way, studies of the TR-OSL together with emission spectroscopy can be helpful in characterizing and identifying the luminescence emission centers [10]. Besides, a dose readout by the TR-OSL technique can be carried out repeatedly without significantly reducing the dose absorbed information of material, unlike CW-OSL. This is important for individual and medical dosimetry.

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In the literature, there are only a few preliminary reports demonstrating a possibility of continuous-wave OSL (CW-OSL) measurements on magnesium aluminum spinels. In particular, CW-OSL emission of pure $MgAl_2O_4$ crystal was reported in Refs. [11,12]. At the same time, a possibility of CW-OSL readout of $MgGa_2O_4$, as well as pulsed OSL (POSL) readout, has not been studied yet. The observation of both TL and OSL signals of the material allows, through the correlation of results, a better understanding of the defects involved in the processes [12]. Also, improvements in the luminescent characteristics of the material can be planned, by considering TL and OSL results.

Therefore, the luminescence of magnesium gallate doped with manganese ions ($MgGa_2O_4$:Mn^{2+}), including TL and TR-OSL properties under irradiation at room temperature with X-ray and beta radiation, have been studied in this research.

2. Experimental

Magnesium gallate ceramics doped with Mn^{2+} ions were synthesized by high-temperature solid-state reaction method. Magnesium oxide (MgO), β-gallium oxide (β-Ga_2O_3) and manganese oxide (MnO) were used as initial materials. All reagents were at least of 4 N grade of purity. Main powders of stoichiometric composition with 0.05 mol.% of MnO (at the expense of MgO) were grinded in an agate mortar for 6 h with further pressing in a steel mold under the pressure of 150 kg/cm^2. Obtained tablets were annealed at 1200 °C for 8 h in the air. These samples were 4 mm in diameter and 1 mm thick.

X-ray diffraction measurements (XRD) 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 ($K_{\alpha 1}$-radiation, $\lambda = 1.5406$ Å). XRD measurements were performed with 0.005° scanning step. Analysis of diffraction peaks was realized with STOE WinXPOW software package.

The photoluminescence excitation (PLE) and photoluminescence (PL) spectra were measured using a CM2203 spectrofluorometer in the 220–820 nm spectral range at room temperature. Excitation of luminescence was performed with a 150 W Xenon lamp. A Hamamatsu R928 photomultiplier was used as luminescence detector. All spectra were obtained with a spectral resolution of 0.5 nm. The registered spectra were automatically corrected by the Xenon lamp emission spectrum and the photomultiplier spectral response.

A setup based on a prism monochromator was applied to study the X-ray luminescence and TL curves. X-ray excitation was done by a microfocus X-ray tube with copper anticathode operated at 45 kV and 0.3 mA. The temperature was monitored using a copper-constantan thermocouple clamped below the sample position. The linear heating regime with the temperature increase rate of 0.2 K/s was provided with a RE-205 microprocessor temperature controller.

Time-resolved OSL (TR-OSL) technique was used to study OSL properties of the material with pulsed stimulation. The TR-OSL measurement system used was described in details by Ref. [10]. Here we used the same measurement setup with some modifications. A green LED ($\lambda_{max} = 525$ nm, power density at the sample position was about 10 mW/cm^2) was used for stimulation. The mechanical shutter in front of the PMT was used for preventing stimulation light reaching the photomultiplier as the emission and stimulation bands overlap. The shutter in front of the PMT was kept closed during the stimulation pulse. The TR-OSL signal was recorded using 0.655 s intervals upon starting of the stimulation pulse of 100 ms width. The TR-OSL emission was registered using a bialkali photocathode PMT (Hamamatsu R268P) working in the photon counting mode with a blue-green bandpass filter in front (490 nm, bandwidth 10 nm). Irradiation of samples was done with a Sr^{90}/Y^{90} beta source at a dose rate at about 27 mGy/s.

3. Results and discussion

3.1. XRD results

X-ray diffraction measurements were performed for $MgGa_2O_4$ samples doped with Mn^{2+} ions. Fig. 1 shows the typical X-ray diffraction pattern of the studied $MgGa_2O_4$:Mn^{2+} sample synthesized at 1200 °C in comparison with the standard pattern (powder diffraction data file ICSD No. 37359). The diffraction analysis confirmed the spinel structure for investigated samples with cubic structure and Fd3m space group (No. 227). An additional diffraction line of low intensity observed at 32.275° is due to the presence of β-Ga_2O_3 phase with a content less than 3 mol%. A similar content of this additional phase was also observed previously for nominally pure and Mn^{2+}–Eu^{3+} co-doped $MgGa_2O_4$ samples obtained by the same technique [2,13]. This β-Ga_2O_3 phase can appear as a result of evaporation of starting materials during annealing of ceramic samples at 1200 °C. The lattice parameter determined for $MgGa_2O_4$:Mn^{2+} is the same as for the undoped $MgGa_2O_4$ and is equal $a = 8.2704$ (1) Å. It should be noted that Mn^{2+} ions occupy mainly tetrahedral positions replacing in the spinel structure the Mg^{2+} cations of similar ionic radii and the same oxidation state. The authors of [1] also report the Ga_2O_3 additional phase at the $MgGa_2O_4$ ceramic synthesizing. At the same time, the phase composition obtained through Rietveld analysis was 89.37% in mass for $MgGa_2O_4$ and 10.63% in mass for Ga_2O_3 [1].

3.2. Photoluminescence studies

The photoluminescence emission and excitation spectra of the $MgGa_2O_4$:Mn^{2+} phosphor are shown in Fig. 2. An intense broad excitation band in the 230–250 nm spectral range as well as more weak bands in the 250–460 nm range (Fig. 2, curve 1) were found in the excitation spectrum of Mn^{2+} ions in $MgGa_2O_4$:Mn^{2+} at 505 nm registration. The intense band near 235 nm belongs to "band-to-band" transitions and may indicate recombination mechanism of Mn^{2+} ions excitation. Similar results were presented in Ref. [13]. The short-wavelength excitation band in the paper [5] is due to host-lattice absorptions. A shoulder at about 270 nm most

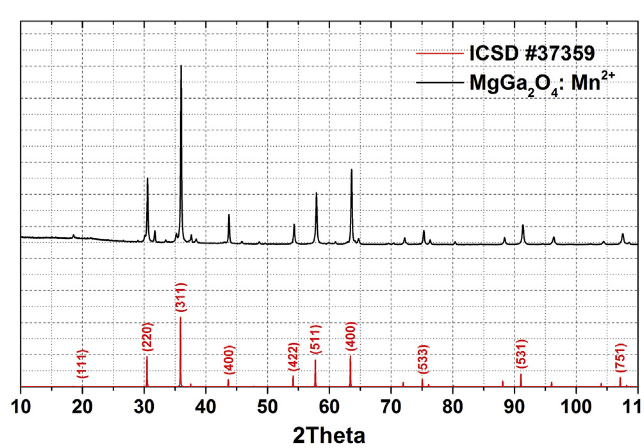

Fig. 1. XRD pattern of $MgGa_2O_4$ doped with 0.05 mol.% MnO synthesized by the high-temperature solid-state reaction method at the 1200 °C and standard diffraction pattern ICSD №37359.