Optical Properties of Hydrogen-Containing MgO Crystal

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ABSTRACT

The photoluminescence (PL), its excitation (PLE) and absorption spectra in ultraviolet, visible and infrared (UV-VIS-IR) regions were used to investigate the MgO single crystals irradiated by fast neutrons. It is shown that the photoluminescence band of the MgO crystals at 730 nm belongs to the hydrogen-containing complex centers V^{-}_{OH}-Fe^{3+}, which are transformed during the irradiation with fast neutrons. The behavior of the PL band 730 nm after fast neutron irradiation depends on the iron-chromium concentration. It is found that the fast neutron irradiation produces the interstitial proton H^{+}_{i} and the $Mg(OH)_2$ microphase.

Keywords: neutron irradiation, absorption spectra, photoluminescence, magnesium oxide;

1. INTRODUCTION

Magnesium oxide is used as a protective layer in plasma display panels, in laser systems and as a substrate material. MgO is a perspective material for the neutron dosimetry. Optical properties of crystals can be essentially modified by presence of impurity ions and radiation induced defects. Hydrogen strongly enhances the formation of radiation defects in MgO lattice because they form different hydrogen-containing complexes and have remarkable influence on crystal properties [1-3]. The source of hydrogen is the moisture absorbed by MgO powder prior to crystal growth [4]. It is known that the absorption spectra of the neutron irradiated MgO consists of four bands with maxima ~250, 355, 573 and 975 nm, associated with radiation defects [5-8]. The absorption spectrum of the MgO crystal, containing impurities of transition elements such as chromium, iron, manganese, shows a bands caused by the d-d transition of these ions [9,10]. The two absorption bands at 280 and 217 nm are associated with Fe^{3+} [11]. In MgO there exist three type of the centers connected with Fe^{3+}ions. The tetrahedral center belongs to "isolated" Fe^{3+}ion surrounded by six O^{2-}. The tetragonal and rhombic centers are connected with cation vacancy in the near neighbourhood. In the tetragonal symmetry the cation vacancy is located in the [100] direction to the Fe^{3+}ion, and in rhombic symmetry - in the [110] direction [12]. A band at 217 nm belongs to a complex center V^{-}_{OH}-Fe^{3+}, as shown in [13]. The luminescence spectra of the MgO crystal, containing impurities of transition elements (chromium, iron, manganese) after exposure to the different types of ionizing radiation and ultraviolet light shows bands in blue, orange and red regions [14-19].
In the present paper we have investigated the photoluminescence (PL), its excitation (PLE) and absorption spectra in ultraviolet, visible and infrared (UV-VIS-IR) regions of MgO single crystals irradiated by fast neutrons.

2. EXPERIMENTAL DETAILS

MgO crystals used in this investigation have been grown by the arc fusion method in Russia. The impurities concentration was detected by means of the instrumental neutron activation analysis [20], the results of which are presented in the table 1.
The neutron irradiation was performed at the Latvian 5 MW water-water research reactor. The fluence of fast neutrons with energy > 0.1 MeV was in the range of $10^{13} – 6.8 \cdot 10^{18}$ cm^{-2}. The irradiation temperature did not exceed 350 K. A cadmium filter was used for absorption of thermal neutrons.

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Table 1.
Concentration of impurities (in mass%).

Notation	Cr	Mn	Fe
MgO (I)	$4.4x10^{-3}$	$5.7x10^{-3}$	$9.0x10^{-3}$
MgO (II)	$2.7x10^{-3}$	$5.6x10^{-3}$	$1.2x10^{-2}$
MgO (III)	$3,7x10^{-3}$	$5.6x10^{-3}$	$7.3x10^{-3}$

PL and PLE spectra were measured at room temperature using conventional equipment consisting of two monochromators (one for the excitation wavelength selection, another for analysis of the luminescence spectra; thus the registration of the excitation spectra for the selected luminescence wavelength as well as the registration of the luminescence spectra for the selected excitation wavelength was possible), a deuterium lamp as a continuous wavelength light source and a recording system based on a photoelectron multiplier. The optical absorption spectra were measured using the "Specord 210" (Analytikjena) double-beam spectrophotometer operating in the spectral region of 190-1100 nm and the double-beam spectrophotometer "Specord M-40" (Karl Zeiss Jena) operating in the wavelength region of 200–900 nm (50000–11000 cm^{-1}). The infrared absorption data were taken with a FTIR spectrometer Equinox 55 (Bruker). Optical measurements before and after irradiation were carried out at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 gives the absorption spectra of MgO before and after fast neutron irradiation. Two of the observed bands correspond to oxygen vacancies with one and two electrons: F^+- centers have absorption band at 252 nm and F centers - at 247.5 nm. Neutral anion divacances or F_2 centers have absorption bands at 355 and 975 nm and an unidentified aggregate defect absorbs at 573 nm. Beside we observe two absorption bands associated with Fe^{3+} at 280 and 217 nm.

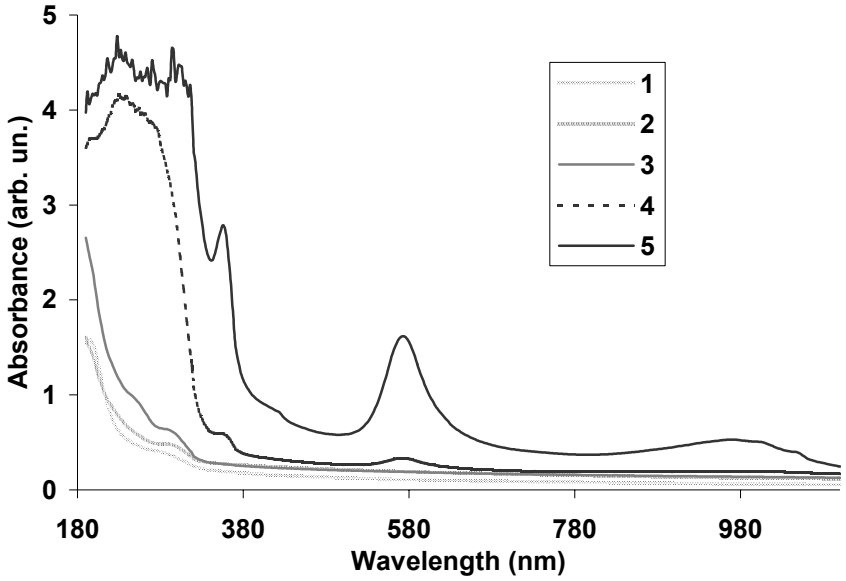

Fig.1. Optical absorption spectra of MgO (III) crystal: 1 - before irradiation;
after fast neutron irradiation with 2 - $\Phi = 10^{14}$ cm^{-2}, 3 - $\Phi = 10^{15}$ cm^{-2}, 4 - $\Phi = 10^{16}$ cm^{-2}, 5 - $\Phi = 10^{18}$ cm^{-2}.

The photoluminescence excitation spectra for the samples, which are nonirradiated and contain different transition ions concentration are shown in Fig. 2 (λ_{lum} = 730 nm). PL excitation spectra of nonirradiated MgO crystal contain 214, 293, 420 and 480 nm bands. The intensity ratio of the 214 nm and 420 nm excitation bands is constant (around 2) for all the studied samples. Excitation in both these bands gives the same luminescence band 720 nm (Fig. 4, curves 1 and 2). This

allows concluding that the 214 nm and 420 nm excitation bands correspond to the excitation of the different energy levels of the same center.

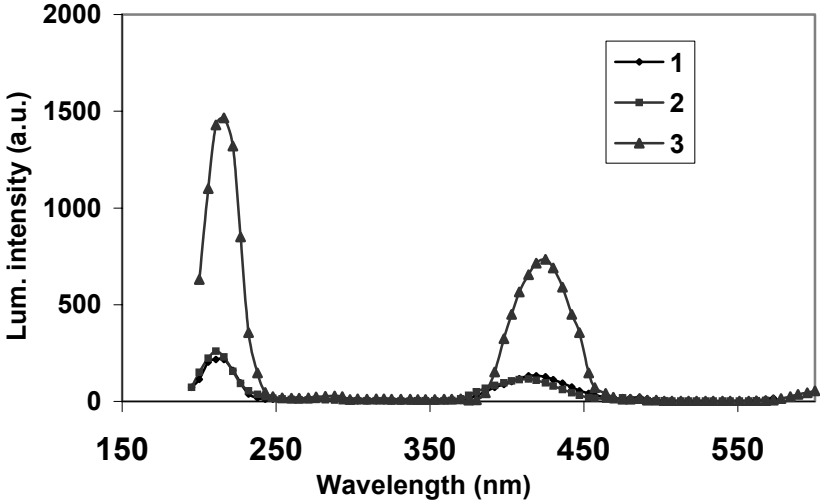

Fig.2. Photoluminescence excitation spectra of nonirradiated crystals:1 - MgO (II), 2 - MgO (I), 3 - MgO (III) (λ_{lum} = 730 nm).

After irradiation the new bands appear in the photoluminescence excitation spectra around 250 nm and 357 nm. Figure 3 shows the PL excitation spectra before and after irradiation with fast neutrons at different fluence. The increase of the fluence leads to the decrease of intensities of the bands at 214 and 420 nm.

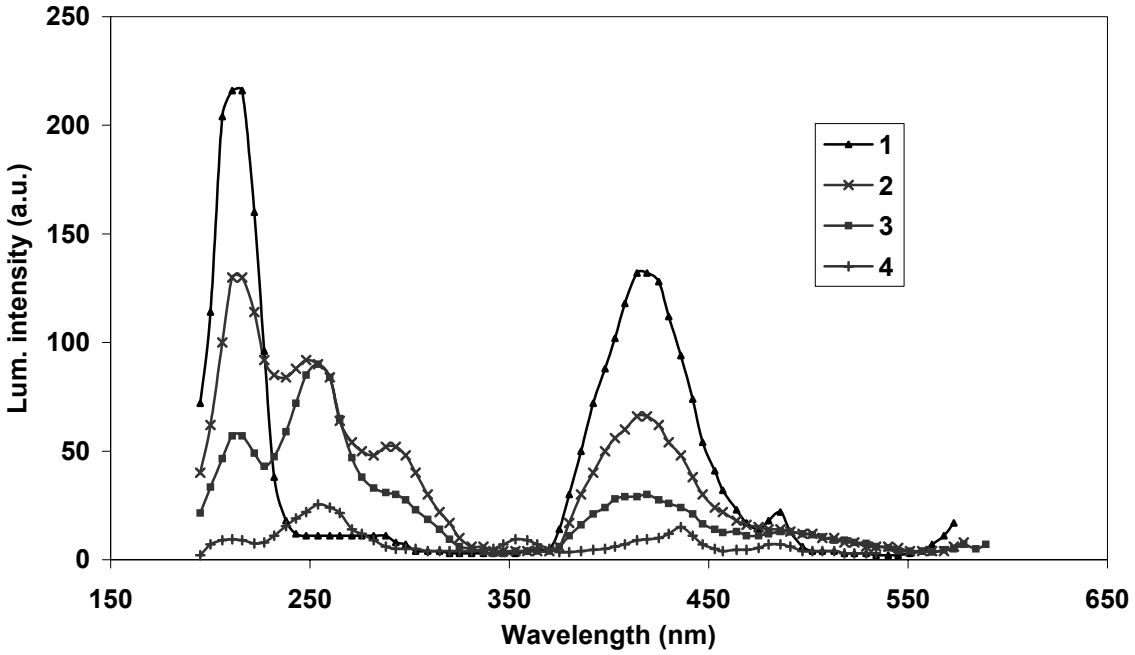

Fig.3. Photoluminescence excitation spectra of MgO (II) crystals: 1 - nonirradiated, 2 - irradiated by fast neutron fluence $\Phi=10^{14}$ cm^{-2}, 3 - $\Phi=10^{15}$ cm^{-2}, 4 - $\Phi=10^{16}$ cm^{-2}.

The photoluminescence spectra of MgO crystals with different concentration of transition ions before and after fast neutron irradiation at λ_{ex}=214 nm are shown in Fig. 4, 5. The behaviour of the PL band with increase of the fast neutron fluence depends upon the concentration of transition ions. The crystal containing the greater concentration of iron has the more symmetric band with the clearly pronounced maximum at 720 nm, whereas for the samples with the low iron

content the band's maximum is shifted with fluence increase. Probably in this case one should take into consideration the ratio of iron and chromium. For MgO (I) it is ~2:1, for MgO (II) – 4:1 and for MgO (III) – 2:1.

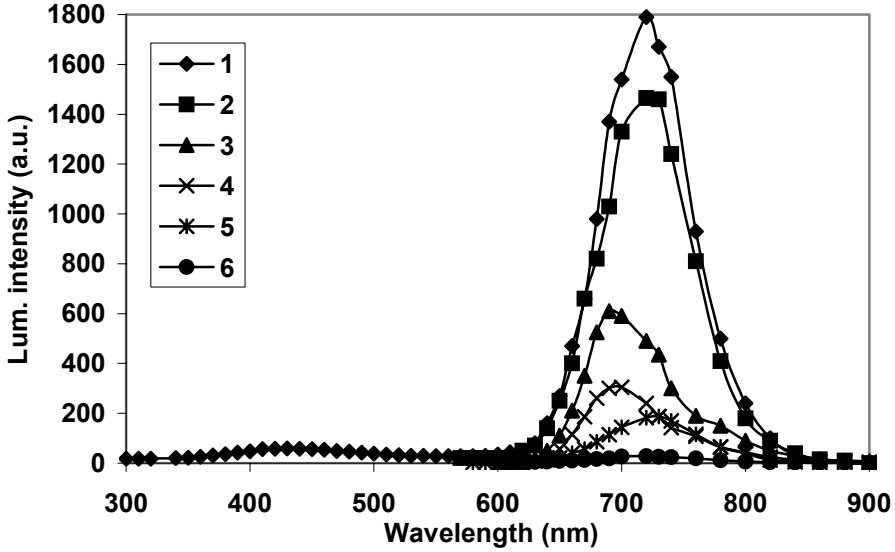

Fig.4. Photoluminescence spectra of MgO (I): 1 - nonirradiated, λ_{ex}=214 nm, 2 - nonirradiated, λ_{ex}=420 nm, 3-6. irradiated by fast neutron fluence, λ_{ex}=214 nm, 3 - $\Phi=10^{14}$ cm^{-2}, 4 - $\Phi=10^{15}$ cm^{-2}, 5 - $\Phi=10^{16}$ cm^{-2}, 6 - $\Phi=10^{18}$ cm^{-2}.

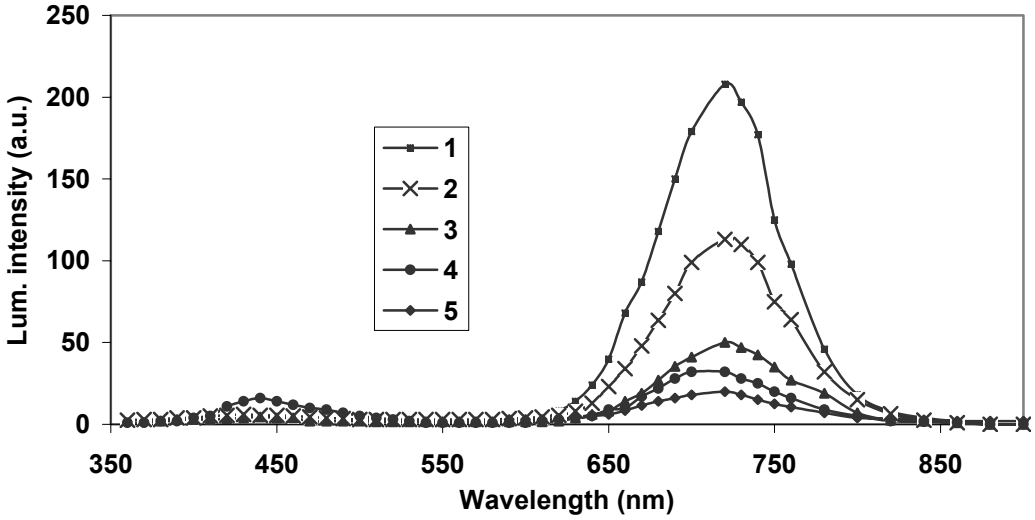

Fig.5. Photoluminescence spectra of MgO (II) λ_{ex}=214 nm: 1 - nonirradiated; irradiated by fast neutron fluence 2 - $\Phi=10^{14}$ cm^{-2}, 3 - $\Phi=10^{15}$ cm^{-2}, 4 - $\Phi=10^{16}$ cm^{-2}, 5 - $\Phi=10^{18}$ cm^{-2}.

The photoluminescence spectra of MgO crystals (both nonirradiated and irradiated) contain the dominating feature centered at 720 nm and a weak band with a maximum at 430 nm. It has been found that the position of the long wavelength emission band depends on the excitation wavelength. The photoluminescence spectra of MgO crystals irradiated by fast neutrons with fluence $\Phi=10^{15}$ cm^{-2} at different excitation wavelengths are given in Fig. 6. The bands with maxima 650, 610, 440 and 410 nm appear after irradiation. The long wavelength emission band is complex, it consists of 700, 730 and 760 nm subbands. The intensity of the ~720 nm PL band decreases with the increasing fluence. Summarizing the results, the following mechanisms are proposed. The red emission in MgO has been associated with Cr^{3+} [21] arising from the following process:

$$Cr^{2+} + \text{hole} \rightarrow Cr^{3+} + h\nu \text{ (R line – 700 nm)}.$$

Clement and Hodgson [15] show that the red emission around ~700 nm is not entirely due to Cr^{3+}, and point to Fe^{2+} as the most likely source. Moreover, an interaction between the Fe and Cr ions can occur, in which Cr^{3+} acts as an electron trap:

$$Fe^{2+} + Cr^{3+} \rightarrow Fe^{3+} + Cr^{2+}.$$

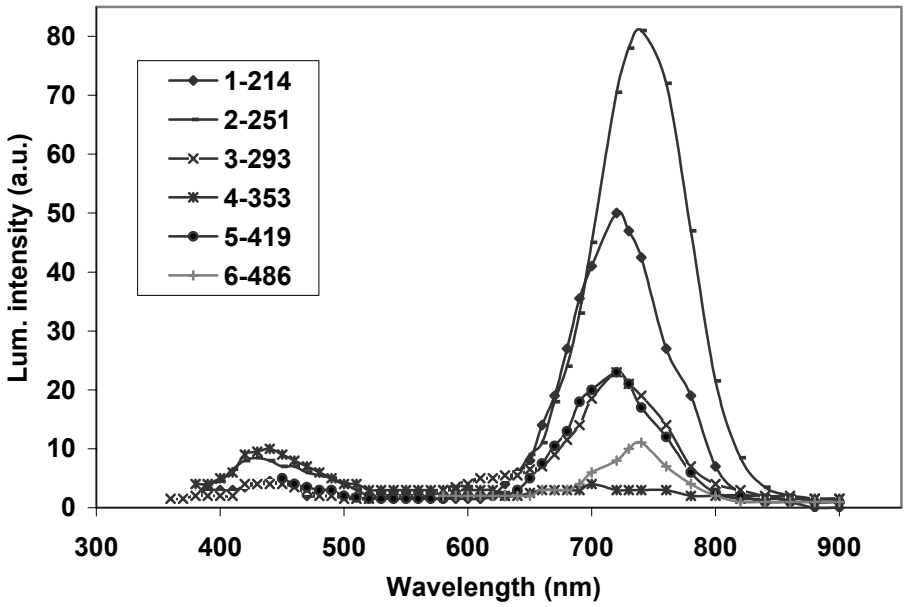

Fig.6. Photoluminescence spectra of MgO (II) crystal irradiated by fast neutrons with fluence $\Phi=10^{15}$ cm^{-2} at different excitation wavelengths.

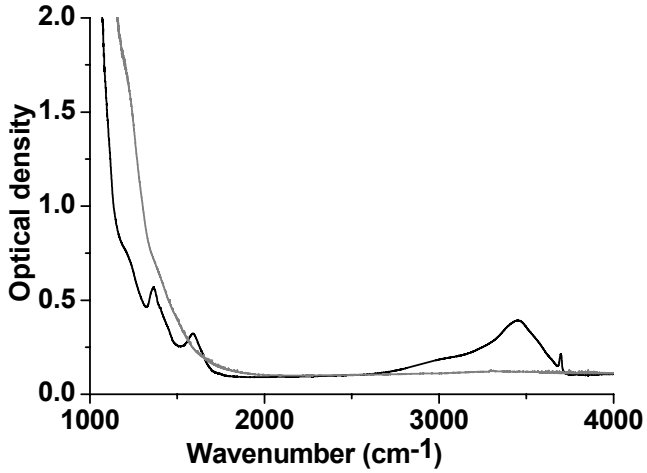

Fig. 7. Infrared absorption spectra of MgO crystal irradiated by fast neutrons: grey line - fluence $\Phi=10^{16}$ cm^{-2}, black line - $\Phi=10^{18}$ cm^{-2}.

For the neutron irradiated MgO crystals the wide luminescence band ~652,5 nm and zero-phonon lines ~649 nm correspond to the complex impurity-vacancy centers "Mn^{2+}-F^{+} (or F) center" [10]. The excitation spectrum of luminescence correlates well with the observed absorption spectrum [13] of MgO, which is assigned to the complex V^{-}_{OH}-Fe^{3+} center. We suggest that the fluence increase involves the next processes:

$$Fe^{2+} + \text{hole} \rightarrow Fe^{3+} + h\nu \text{ (610 nm)};$$
$$Fe^{2+} + \text{hole} \rightarrow Fe^{3+} + h\nu \text{ (410 nm)};$$
$$V^{-}_{OH}\text{-}Fe^{3+} + e^{-} \rightarrow V^{-}_{OH}\text{-}Fe^{2+} + h\nu \text{ (730 nm)}.$$

We assume that the 730 nm photoluminescence band of the MgO crystals belongs to the complex V^{-}_{OH}-Fe^{3+} centers, which are transformed during the irradiation with fast neutrons. The blue emission at 410 nm can be attributed to transition in Fe^{3+} at slightly different local symmetry [16]. The V^{-} and V centers observed in the neutron irradiated crystals at fluence ~10^{18} cm^{-2} are produced as a result of the displacement of protons from V_{OH} sites. After the fluence increasing the following reactions can occur:

$$V^{-}_{OH} + h^{+} \rightarrow V_{OH};$$
$$V_{OH} \rightarrow V^{-} + H^{+}_{i};$$
$$2V_{OH} + e^{-} \rightarrow V^{-} + V_{(OH)2}.$$

Fig. 7 shows the IR spectra of MgO crystals for the different fluences of fast neutrons. It is well established that the OH^{-} stretching frequency is located at 3296 cm^{-1} for the V^{-}_{OH} center and at 3323 cm^{-1} for the V_{OH} center. The bands at 3340 and 3375 cm^{-1} have been attributed to V^{-}_{OH} centers perturbed by the nearest impurities. In the infrared absorption spectra the 3400 cm^{-1} band is assigned to the interstitial proton H^{+}_{i} while the 3700 cm^{-1} band is attributed to a microphase $Mg(OH)_2$ [22]. At the fluence $10^{18}cm^{-1}$ we observe the bands, which are connected with interstitial proton and microphase $Mg(OH)_2$.

4. CONCLUSIONS

The photoluminescence (PL), its excitation (PLE) and absorption spectra in ultraviolet, visible and infrared (UV-VIS-IR) region of the MgO single crystals irradiated by fast neutrons are investigated. It is shown that the 730 nm photoluminescence band of the MgO crystals belongs to the hydrogen-containing complex centers V^{-}_{OH}-Fe^{3+}, which are transformed during the irradiation with fast neutrons. The behaviour of the PL band ~730 nm after fast neutron irradiation depends on the iron-chromium concentration. The fast neutron irradiation produces the interstitial proton H^{+}_{i} and the $Mg(OH)_2$ microphase.

ACKNOWLEGMENTS

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