The Optical Properties of Magnesium Oxide Containing Transition Metal Ions and Defects Produced by Fast Neutron Irradiation

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Abstract: - The photoluminescence (PL), its excitation (PLE) and optical absorption of MgO crystals containing transition metal ions and defects produced by fast neutron irradiation fluence up to $10^{20} \mathrm{cm}^{-2}$ (E>0.1 MeV) are investigated. Three range of luminescence are observed: 380-460 nm, 650-850 nm and 850-1050 nm. These luminescence bands are attributed to presence of Fe^{3+}. We assume that the 440 nm photoluminescence band belongs to the complex V^-_{OH}-Fe^{3+} center with tetragonal symmetry, while the ~730 nm PL band observed in the irradiated MgO crystals is connected with defects, generated as a result of decay of the complex V^-_{OH}-Fe^{3+} centers. The near infrared luminescence bands in MgO crystal are connected with the Fe^{3+}- Fe^{3+} exchange coupled pairs. Furthermore the luminescence of chromium and manganese ions of different symmetry is observed.

Key-Words: - Magnesium oxide, transition metal ions, radiation defect, absorption and luminescence spectra

1 Introduction

Magnesium oxide is one of the most representative materials among the oxides for important technological application thanks to its wide bandgap (7.8 eV) and a good chemical and thermal (melting points is 2800ºC) stability [1-5]. In the same time MgO with its simple rock-salt structure is one the most significant metal oxides for theoretical and experimental studies. Optical properties of crystals can be essentially modified by the presence of impurity ions and radiation induced defects. These impurity ions can be used as a probe for understanding of defects structure. MgO has a very simple lattice which can be a host for a number of transition metal ions. The local structure around the added metals plays an important role for the catalytic properties of the modified MgO samples.

Point defects and trace impurities in crystals are often a key point in the energy transfer and storage process and may influence the material performance significantly. Apart from raw material contamination and intrinsic point defects (such as oxygen vacancies or O^- small polarons [6]); also the technology of crystal growth may contribute to material imperfections in many aspects.

2 Problem Formulation

The most common defects encountered in neutron irradiated MgO are anion vacancies [7]. Anion vacancies occur in two charge states: F^+ and F centers, corresponding to oxygen vacancies with one and two electrons, respectively. F^+- centers have absorption band at 252 nm (4.92 eV) and F centers - at 247.5 nm (5.01 eV) and corresponding photoluminescence bands are at 387 nm (3.2 eV) and 540 nm (2.3 eV), respectively. Neutral anion divacances or F_2 centers have absorption bands at 355 and 975 nm (3.49 and 1.27 eV) and an unidentified aggregate defect absorbs at 573 nm (2.16 eV).

The second common type of defects in MgO is V-type centers. The simplest of these consists of one hole trapped at the Mg^{2+} ion vacancy with the hole being shared with the next-neighbour oxygen. The absorption spectrum of MgO crystal, containing impurities of transition elements such as chromium, iron, manganese, shows a band caused by the d-d transition of these ions [8, 9]. The two absorption bands at 280 and 217 nm have been reported earlier [10] to be associated with Fe^{3+}. A band at 217 nm belongs to a complex center V^-_{OH}-Fe^{3+}, as shown in [11]. The luminescence spectra of MgO crystal, containing impurities of transition elements (chromium, iron,

manganese) show bands in the blue, orange and red regions after exposure to different types of ionizing radiation, including ultraviolet light [12-17].

The current understanding of the role of transition metal impurities in the optical absorption and photoluminescence in MgO is not yet completely established, particularly in relation to the effect of neutron irradiation in this material.

In this paper we present the results of investigation of the optical properties of magnesium oxide containing transition metal ions and defects produced by fast neutron irradiation.

3 Problem Solution

MgO crystals used in this investigation have been grown by the arc fusion method in Russia. The samples' thickness was in the range of 0.5–1 mm.

The impurity concentration was detected by means of the instrumental neutron activation analysis [18].

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

	Cr	Fe	Mn
MgO(1)	3.7×10^{-3}	7.3×10^{-3}	5.6×10^{-3}
MgO(2)	4.4×10^{-3}	9.0×10^{-3}	5.7×10^{-3}
MgO(3)	2.7×10^{-3}	1.2×10^{-2}	6.5×10^{-3}
MgO(4)	1.8×10^{-4}	4.3×10^{-2}	2.4×10^{-4}

The neutron irradiation was performed at Latvian 5 MW water-water research reactor. The fluence of fast neutrons with energy > 0.1 MeV was in the range of $10^{14} - 10^{20}$ cm^{-2}. The irradiation temperature did not exceed 350 K. Cadmium filter was used for absorption of thermal neutrons.

PLE spectra were measured at room temperature using conventional equipment consisting of two monochromators (one for selection of excitation wavelength, another for detection of the luminescence spectra; thus the registration of the excitation spectra for the selected luminescence wavelength as well the registration of the luminescence spectra for the selected excitation wavelength was possible), a deuterium lamp as a light source with continuous wavelength. PL spectra were measured using ANDOR grating monochromator combined with CCD camera. 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.

It is known that the absorption spectra of the neutron irradiated MgO consists of four bands with maxima at ~250, 355, 573 and 975 nm, associated with radiation defects [6, 19-21]. Fig. 1 gives the absorption spectra of MgO before and after fast neutron irradiation.
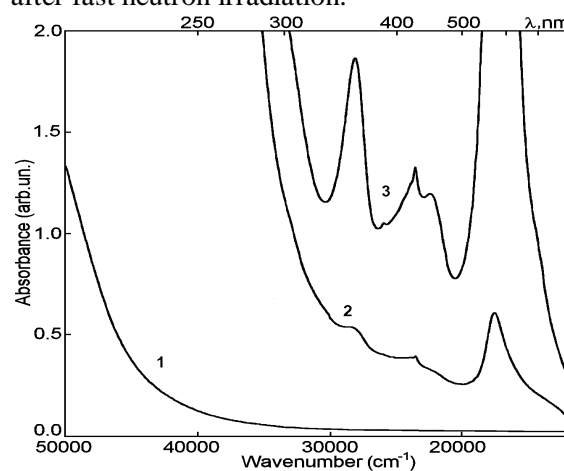

Fig.1. Optical absorption spectra of MgO (4) crystal: 1 - before irradiation, 2 - after fast neutron irradiation $\Phi = 10^{16}$ cm^{-2}, 3 - $\Phi = 10^{20}$ cm^{-2}.

The photoluminescence excitation spectra for the samples, which are nonirradiated and contain different transition ions concentration are shown in Fig. 2 ($\lambda_{lum} = 730$ 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 these both bands gives the same luminescence band 720 nm. 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. After irradiation the new bands appear in the photoluminescence excitation spectra around 250 nm and 357 nm [22]. The increase of the fluence leads to the decrease of intensities of the bands at 214 and 420 nm.
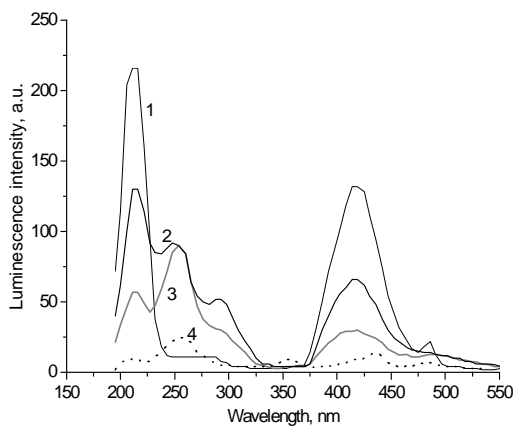
Fig.2. Photoluminescence excitation spectra of MgO crystals: 1. nonirradiated, 2. irradiated with fast neutron fluence $\Phi=10^{14}\,cm^{-2}$, 3. $\Phi=10^{15}\,cm^{-2}$, 4. $\Phi=10^{16}\,cm^{-2}$.

Three ranges of luminescence are established: 380-460 nm, 650-850 nm and 850-1050 nm in the most part of the investigated samples excited at the given above wavelengths. The photoluminescence spectra of MgO crystals irradiated by fast neutrons with fluence $\Phi=10^{18}\,cm^{-2}$ at different excitation wavelengths and different impurities concentration are given in Figure 3 – 4. Analysis shows that the intensity of emission in each of these regions is strongly dependent on concentration of transition metal ions, temperature of annealing and irradiation conditions. The crystal containing the larger concentration of iron has the more symmetric band with clearly pronounced maxima at 720 nm, whereas for the samples with the low iron content the bands maxima are 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 (3) - 4:1 and for MgO (2) –2:1.

The red emission band is complex, it consists of 700, 730 and 760 nm subbands. In addition, we observed sharp lines, which belong to the R and N-lines of Cr^{3+} ions [18]. The chromium ions in crystals are coordinated by neighbor oxygen ions and characterized by different possible charge states in crystal lattices. The $3d^3$ ions has been shown to occupy lattice sites with different symmetries because of the need for charge compensation. Many of the Cr^{3+} ions substitute for Mg^{2+} ions without local charge compensation; these ions occupy octahedral symmetry sites.

However, since there is charge compensation in the form of one cation vacancy for every two Cr^{3+} ions, some trivalent ions are observed in noncubic sites. Particularly, if the charge compensating vacancy occupies a nearest-neighbour or next-nearest-neighbour site to the Cr^{3+} ion then the point symmetry is orthorhombic or tetragonal, respectively.
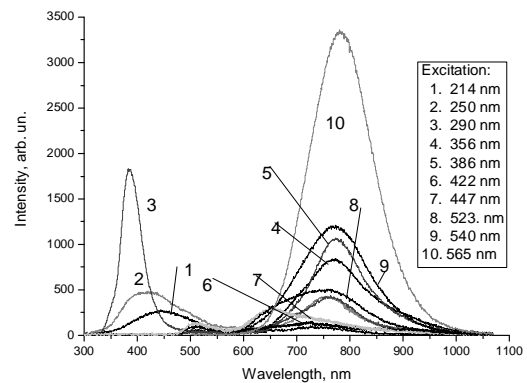

Fig. 3. Photoluminescence spectra of MgO (4) crystal irradiated by fast neutrons with fluence $\Phi=10^{18}\,cm^{-2}$ at different excitation wavelengths
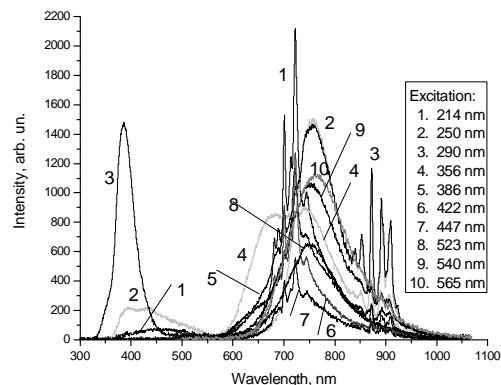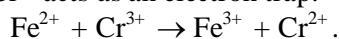

Fig. 4. Photoluminescence spectra of MgO (1) crystal irradiated by fast neutrons with fluence $\Phi=10^{18}\,cm^{-2}$ at different excitation wavelengths.

For the neutron irradiated MgO crystals the wide luminescence band ~652,5 nm (1.9 eV) and zero-phonon lines ~ 649 nm (1.91 eV) correspond to the complex impurity-vacancy defect "Mn^{2+}-F^+ (or F) center" [8].

Three types of electronic transitions occur in MgO, containing transition metal ions such as Fe. First, there are the Fe^{3+} ligand field transitions; second, there is the ligand to metal charge-transfer transition; third, there is the transition which results from the simultaneous excitation of

magnetically–coupled Fe^{3+} cations, which occupy adjacent sites. The octahedral centre complies with an "isolated" Fe^{3+} ion surrounded by six O^{2-}. The tetragonal and rhombic centres are connected with cation vacancies in the near neighbourhood. In the tetragonal symmetry, the cation vacancy is located in the [100] direction, and in rhombic symmetry - in the [110] direction regarding the Fe^{3+} ion. At low concentration iron is present in a form of Fe^{2+} and Fe^{3+} and may be transformed from one valence state to another by ionizing radiation, due to an electron capture on other impurities or by reduction or oxidation at high temperatures. The excitation spectrum of luminescence correlates well with the observed absorption spectrum. A band at 217 nm belongs to a complex center V^-_{OH}-Fe^{3+}, as shown in [10]. The increase of fluence leads to the release of holes and their capture by Fe^{2+}, producing Fe^{3+} luminescence. The excess charge is compensated by cation vacancy. We assume that the 440 nm photoluminescence band belongs to the complex V^-_{OH}-Fe^{3+} center with tetragonal symmetry, and the ~730 nm PL band observed in the irradiated MgO crystals is connected with defects, generated as a result of decay of the complex V^-_{OH}-Fe^{3+} centers. Moreover an interaction between the Fe and Cr ions can occur, in which Cr^{3+} acts as an electron trap:

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

The photoluminescence spectra of MgO (1) show the sharp lines after irradiation with fast neutrons in the 850-950 nm regions. Essential distinctions of this crystal from other investigated crystals is absence of the 3700 cm^{-1} band in IR absorption spectra connected with the $Mg(OH)_2$ micro phase formation (Fig. 5-6).
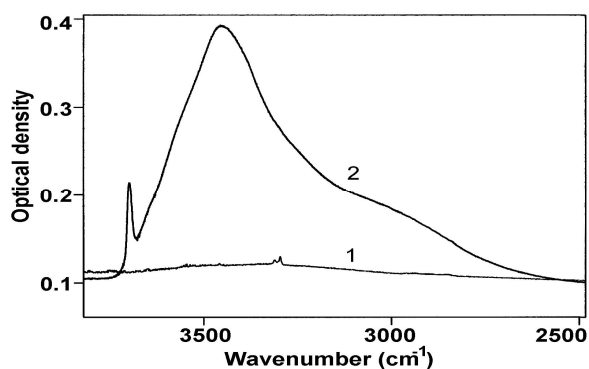

Fig. 5. Infrared absorption spectra of MgO (3) crystal irradiated by fast neutrons: 1. fluence $\Phi=10^{16}\,cm^{-2}$, 2. $\Phi=10^{18}\,cm^{-2}$.
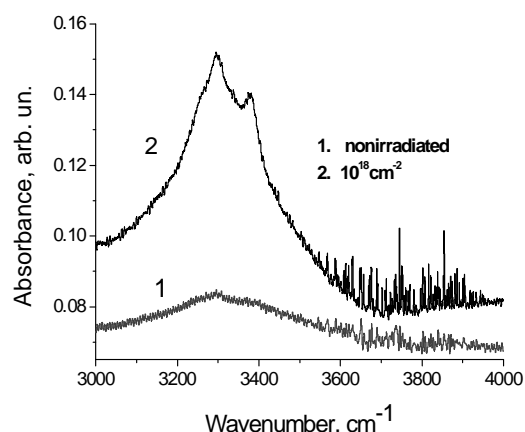

Fig. 6. Infrared absorption spectra of MgO (1) crystal irradiated by fast neutrons: nonirradiated, 2. $\Phi=10^{18}\,cm^{-2}$.

The red band's intensity in this crystal decreases after irradiation because the total concentration of V^-_{OH}-Fe^{3+} centres is small. The fine structure in PL spectra has been observed under excitation in iron absorption bands. Probably the adjacent Fe^{3+} cations may form an exchange coupled pair in the absence of hydroxyl groups in the nearest neighbourhood, which causes appearance of the sharp lines in the 850-950 nm region.

4 Conclusion

The photoluminescence (PL), its excitation (PLE) and optical absorption of MgO crystals contained transition metal ions and defects produced by fast neutron irradiation fluence up to $10^{20}\,cm^{-2}$ (E>0.1 MeV) are investigated. Three range of luminescence are observed: 380-460 nm, 650-850 nm and 850-1050 nm. These luminescence bands are attributed to presence of Fe^{3+}. We assume that the 440 nm photoluminescence band belongs to the complex V^-_{OH}-Fe^{3+} center with tetragonal symmetry, while the ~730 nm PL band observed in the irradiated MgO crystals is connected with defects, generated as a result of decay of the complex V^-_{OH}–Fe^{3+} centers. The near infrared luminescence bands in MgO crystal are connected with the Fe^{3+}- Fe^{3+} exchange coupled pairs. Furthermore the luminescence of chromium and manganese ions of different symmetry is observed.

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