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Transient and stable color centers in neutron irradiated MgO

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Abstract

The transient absorption and luminescence induced by the pulsed electron beam have been investigated in the MgO single crystal containing transition metal ion (Cr, Mn, Fe) impurities and preliminary irradiated by the fast neutrons. It is supposed that the different behavior of the absorption spectra of the MgO samples preliminary irradiated by the different fast neutron fluence is connected with the destruction of the hole centers and with the creation of interstitial protons and the formation of the microphase $Mg(OH)_2$. We assume that the luminescence band at ~3.2 eV is connected with F^+ color centers.

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Keywords: Neutron irradiation; Absorption spectra; Photoluminescence; Magnesium oxide

1. Introduction

Magnesium oxide has numerous technological applications. This material is used in advanced systems for energy conversion as a refractory insulator [1], in laser systems [2] and as a substrate material [3,4]. MgO is a perspective material for the neutron dosimetry [5–7]. The presence of the transition metal impurities in refractory oxides such as magnesium oxide affects quite markedly the optical, electrical and mechanical properties. It is known [8–16] that the absorption spectra of the neutron irradiated MgO consist of several bands, associated with radiation defects. F^+ and F centers (oxygen vacancies with one and two electrons, respectively) absorb at nearly the same energy 4.92 and 5.1 eV (252 and 247 nm). Neutral divacancies or F_2 centers absorb at 3.47 and 1.27 eV (355 and 975 nm) and unidentified aggregate defect absorbs at 2.16 eV (573 nm). In addition to the above-mentioned bands spectra display bands at 5.7, 5.2, 4.3 eV and a few bands in the region from 3.2 to 2.8 eV, which are due to the transition metal ions. As shown in [17] a band at 5.7 eV (217 nm) belongs to a complex center V^-_{OH}–Fe^{3+}. Depending on the life time the color centers (CC) in oxide crystals can be divided into stable color centers (SCC) existing in crystals in the time range from a second to a few months or years, and transient color centers (TCC) with the life time less than one second after the ceasing of excitation. This paper presents the investigations of the transient (TCC) and stable (SCC) color centers in MgO, containing the transition metal ion (Cr, Mn, Fe) impurity, preliminary irradiated by the fast neutrons.

2. Experimental

The MgO crystals used in this investigation have been grown by the arc fusion method in Russia. The concentration of impurities was detected by means of the instrumental neutron activation analysis [18]. The investigated MgO crystals contain: Cr – 4.4×10^{-3}, Mn – 5.7×10^{-3}, Fe – 9.0×10^{-3} wt%. The neutron irradiation was performed at the Latvian 5 MW water–water research reactor. The fluence of the fast neutrons with energy >0.1 MeV was in the range of 10^{13}–6.8×10^{18} cm^{-2}. The irradiation temperature did not exceed 350 K. A cadmium filter was used for

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the absorption of the thermal neutrons. The transient absorption and luminescence spectra of the MgO crystals preliminary irradiated by the fast neutron were measured. The TCC was induced by the pulsed electron beam (the pulse duration 10 ns, the average density of electron beam 10^{12} el/cm^2, the electron beam energy 270 keV). The experimental procedure of measuring the transient absorption induced by electron beam is presented in details in [19].

The infrared absorption experiment was performed with a FTIR spectrometer Bruker Equinox 55. The optical measurements before and after the neutron irradiation were carried out at room temperature.

3. Results and discussion

The transient absorption induced by electrons in the MgO single crystal, preliminary irradiated by the fast neutrons at fluence 10^{16} cm^{-2} and 10^{18} cm^{-2}, is depicted in Fig. 1. It is shown that a wide transient absorption band with two maxima in the region ~2.5 eV and ~3.5–4 eV appears in the MgO crystal preliminary irradiated by the fast neutrons at fluence 10^{16} cm^{-2}. The fast neutron fluence increasing up to 10^{18} cm^{-2} leads to the appearance of two bands in the transient absorption spectra with the maxima at ~2.7 and ~1.8 eV. The intensity of these bands decreases slowly, less than 15% in 8000 ns. Since the spectral region of the TCC absorption ~3.4–4 eV in the MgO single crystal, preliminary irradiated by the fast neutrons at fluence 10^{16} cm^{-2} and ~1.8 eV (10^{18} cm^{-2}) is practically identical to the absorption band of the stable center described in [8,20–23], one can suppose that transient absorption in this region is associated with the F_2-center (~3.47 eV) and with the transition ion (Cr, Mn, Fe) impurities.

The band at ~2.5 eV for the sample irradiated by fast neutron fluence 10^{16} cm^{-2} is probably composed of several bands. The main contribution for this band is given by the hole centers V^- and V_{OH} with maxima ~2.3 eV. The radiation-induced absorption band at 2.3 eV has been described by Wertz et al. [24–26]. We assume that in the irradiated crystal containing V^-_{OH} and V^-_{OH}–Me^{2+} centers (where Me = Cr, Mn, Fe) at small fluence V_{OH} centers arise as a result of the trapping of the holes

$$V^-_{OH} + h^+ \rightarrow V_{OH},$$
$$V^-_{OH}\text{–}Me^{2+} + h^+ \rightarrow V^-_{OH}\text{–}Me^{3+}.$$

The V^- and V^o centers observed in the neutron irradiated crystals at fluence ~10^{18} cm^{-2} are produced as a result of the displacements of protons from V_{OH} sites. After the fluence increasing the following reactions can occur:

$$V_{OH} \rightarrow V^- + H^+_i,$$
$$2V_{OH} + e^- \rightarrow V^- + V_{(OH)_2}.$$

The Fig. 2 shows the IR spectra of the MgO crystals irradiated at different fluence of fast neutrons. At the fluence 10^{16} cm^{-2} two narrow bands 3296 and 3318 cm^{-1} emerge. Fluence increasing to 10^{18} cm^{-2} gives rise to the wide band at ~3400 cm^{-1} and the narrow band 3700 cm^{-1}. 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 $Mg(OH)_2$ [27,28]. The increase of the neutron fluence leads to the decay of the V_{OH} centers with the generation of an interstitial proton $H^+$and a microphase $Mg(OH)_2$. The obtained results confirm our suggestion about the hole nature of the centers responsible for the observed absorption bands.

The luminescence spectra of the MgO single crystals irradiated by a pulse electron beam are shown in the Fig. 3. The MgO single crystals preliminary irradiated by the fast neutrons were used in this investigation. Two wide

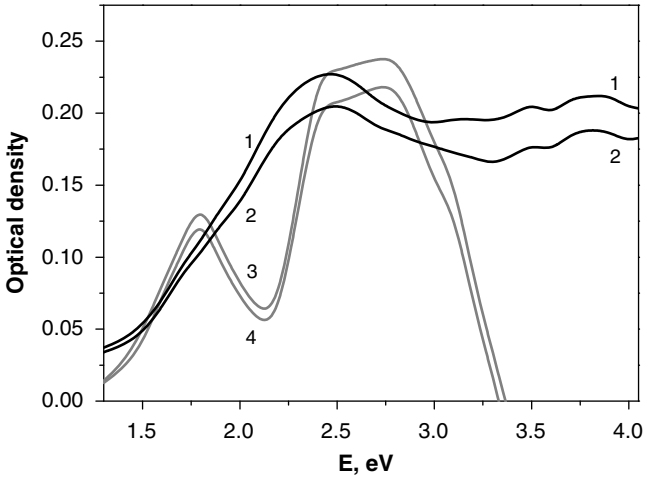

Fig. 1. The spectra of the transient optical density induced by electrons in the MgO single crystals, preliminary irradiated by the fast neutrons: (1) fluence 10^{16} cm^{-2}, 20 ns delay after start of the excitation pulse; (2) fluence 10^{16} cm^{-2}, 5000 ns delay; (3) fluence 10^{18} cm^{-2}, 20 ns delay after start of the excitation pulse; (4) fluence 10^{18} cm^{-2}, 5000 ns delay.

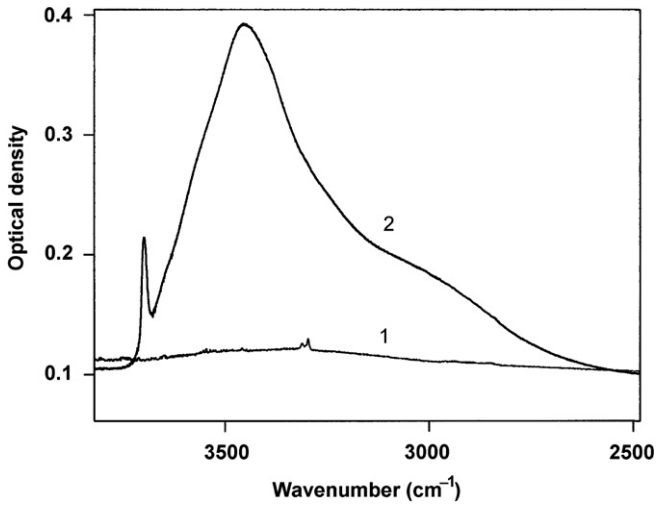

Fig. 2. The infrared absorption spectra of the MgO crystal irradiated by the fast neutrons: (1) fluence $\Phi = 10^{16}$ cm^{-2} and (2) $\Phi = 10^{18}$ cm^{-2}.

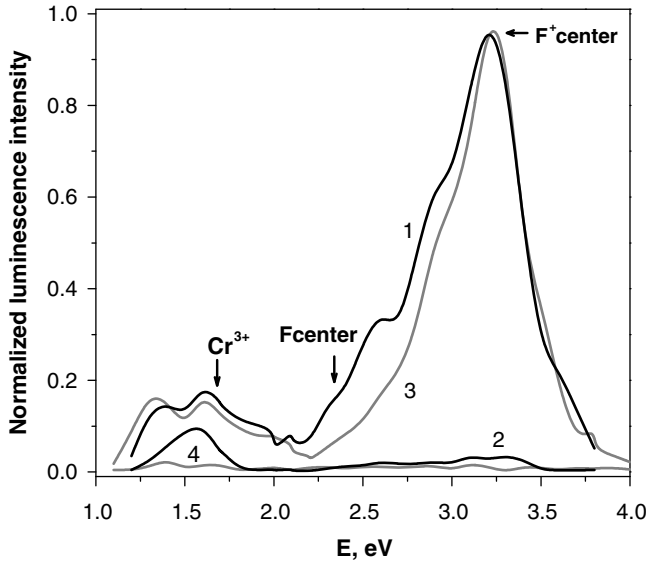

Fig. 3. The spectra of luminescence excited by the pulsed electron beam in the MgO single crystals, preliminary irradiated by the fast neutrons: (1) fluence 10^{16} cm^{-2}, 20 ns delay after start of the excitation pulse; (2) fluence 10^{16} cm^{-2}, 100 ns delay; (3) fluence 10^{18} cm^{-2}, 20 ns delay after start of the excitation pulse; (4) fluence 10^{18} cm^{-2}, 100 ns delay.

bands at ~3.2 eV and ~1.2–2.0 eV were observed. During the first ~200 ns only a part of the complex band ~1.2–2.0 eV decays, whereas the ~3.2 eV band decays almost completely. The luminescence band ~3.2 eV in the MgO preliminary irradiated by the fast neutron fluence 10^{18} cm^{-2} practically was not observed at the 100 ns delay. The luminescence band at ~1.2–2.0 eV belongs to the transition metal ions. The red emission in MgO has been associated with Cr^{3+} [29,30]. Clement and Hodgson [31] show that the red emission around ~1.75 eV is not entirely due to Cr^{3+}, and point to Fe^{2+} as the most likely source. The Fe^{2+} arising from reaction $Fe^{3+} + e^- \rightarrow Fe^{2+} + h\nu$. Moreover an interaction between the Fe and Cr ions can occur, in which Cr^{3+} acts as an electron trap: $Fe^{2+} + Cr^{3+} \rightarrow Fe^{3+} + Cr^{2+}$. For neutron irradiated MgO crystals the wide luminescence band ~1.9 eV and zero-phonon lines ~1.91 eV correspond to the complex impurity-vacancy centers "Mn^{2+}–F^+ (or F) center" [32]. It is known that the absorption of 5 eV light by the MgO:Mg crystal produces two main emission bands at 3.2 eV and 2.3 eV [33]. The MgO samples excited at 248 nm by the pulsed KBr eximer laser reveal the same bands, which belong to F^+ and F centers [34]. Since the position of the luminescence band at ~3.2 eV is practically identical to the luminescence band described in [33,34] we assume that in our samples this band belongs to the F^+ centers. The F-center contribution to the wide luminescence band at 3.2 eV is very small. The luminescence decay kinetics for the different emission bands is given in the Fig. 4 for the MgO crystal preliminary irradiated by the fast neutron at the fluence 10^{16} cm^{-2}. The life time of the F^+-center is about or smaller than 20 ns and comparable with the results from [34].

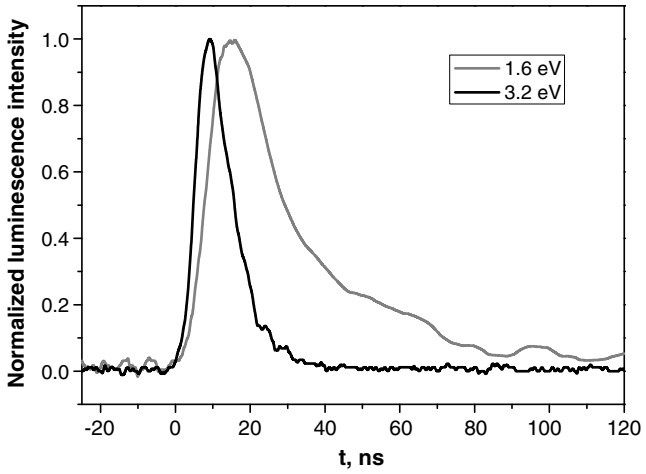

Fig. 4. The luminescence decay kinetics for different emission bands of the MgO crystal (fluence 10^{16} cm^{-2}).

4. Conclusion

The transient and stable color centers were studied in the MgO single crystals containing the transition metal ion (Cr, Mn, Fe) impurity, preliminary irradiated by the fast neutrons. It was found that the behavior of the absorption spectra of the MgO single crystal after the irradiation with the pulsed electron beam depends on the fluence of the neutrons used for the preliminary irradiation of the sample. We believe that increase of the fluence leads to the destruction of the hole centers. As a result, the interstitial protons and microphase $Mg(OH)_2$ are created. We assume that the luminescence band at ~3.2 eV belongs to the F^+ centers.

Acknowledgement

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