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Radiation defects and transition ions interaction in magnesium oxide

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Abstract

The absorption spectra of nickel and manganese doped and pure MgO single crystals were investigated before and after fast neutron irradiation and after annealing. It is shown that the fast neutron irradiation leads to the formation of two types complex center: "Me^{2+}–F^{+} (or F) center" and "Me^{3+}–V_{Mg}". From the behavior of the ~570 and ~357 nm absorption bands during annealing the activation energies of the corresponding defects are determined. The obtained activation energy values ($E_a < 1$ eV) allow us to assume that the transition ions play an important role in the migration of vacancies and interstitials.

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Keywords: Radiation defects; Transition metal oxide; Magnesium oxide

1. Introduction

Magnesium oxide has been the object of experimental and theoretical investigations for many years. This material is utilized in advanced systems for energy conversion as a refractory insulator [1], in laser systems [2] and as a substrate material [3,4]. The presence of impurity ions can determine the main physical and mechanical properties of the MgO crystal [5–7]. It is very important to understand the influence of radiation and temperature on the fundamental properties of these materials. The purpose of the present investigation is to study the interactions between transition ion impurities (nickel and manganese) and the radiation defects produced by fast neutrons in magnesium oxide crystals.

2. Experimental details

MgO crystals used in this investigation have been grown by the arc fusion method in Russia; the single-solid solutions MgO–NiO and MgO–MnO were grown by the chemical transport reaction method [8]. MgO crystals were used as substrates for the single-solid solution growth. The samples thickness was in the range of 0.5–1 mm.

The impurities concentration was detected by means of the instrumental neutron activation analysis [9]. The results are presented in Table 1.

The neutron irradiation was carried out at the Latvian 5MW water–water research reactor. The fluence of fast neutrons with energy >0.1 MeV was in the range 10^{14}–10^{20} cm^{-2}, that of thermal neutrons in the range 10^{14}–2.5×10^{17} cm^{-2}. The accompanying γ-irradiation dose with an average energy 1.1 MeV produced an absorption dose of 0.33 Gy. The range of irradiation temperature was 300–700 K. A cadmium filter was used for absorption of thermal neutrons. The thermal evolution of the absorption bands was observed during the isochronal and isothermal annealing.

The lattice parameter of crystals before and after irradiation was measured with a DRON-UM2 (USSR) diffractometer using CuKα-radiation ($U = 40$ kV, $I = 20$ mA). A computer connected with the diffractometer was used for logging and processing data. Results are presented in Table 2. The optical absorption spectra were measured using the double-beam spectrophotometer "Specord M-40" (Karl Zeiss Jena) operating in the wavelength region of 50,000–11,000 cm^{-1} (200–900 nm). The optical measurements were made in the temperature interval 300–10 K.

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Table 1
Concentration of impurities (in mass%)

Notation	Cr	Fe	Mn	Ni
MgO	1.75×10^{-4}	1.1×10^{-2}	5.8×10^{-3}	$<5\times10^{-5}$
MgO	8.5×10^{-4}	7.3×10^{-4}	$<10^{-5}$	–
MgO	3.7×10^{-3}	7.3×10^{-3}	5.6×10^{-3}	–
MgO	2.7×10^{-3}	1.2×10^{-2}	6.5×10^{-3}	–
MgO:Ni	2×10^{-4}	1×10^{-2}	–	0.35
MgO:Ni	$<3\times10^{-4}$	$<5\times10^{-3}$	–	0.49
MgO:Ni	$<3\times10^{-4}$	1×10^{-2}	–	0.44
MgO:Ni	6.9×10^{-5}	5.1×10^{-4}	2.7×10^{-4}	1.7×10^{-4}

Table 2
Lattice parameters before and after neutron irradiation (a, nm)

Notation	MgO	MgO:Ni	MgO:Ni	MgO:Ni	NiO
Before irradiation	0.4211	0.42080	0.42090	0.42102	0.4177
After fast Φ $10^{17}\,cm^{-2}$	–	0.42050	0.42055	0.42088	–
Thermal Φ $2.5\times10^{17}\,cm^{-2}$	–	–	–	0.42043	–
After annealing	–	0.42086	–	–	–

3. Results and discussion

It is known that the absorption spectra of the neutron irradiated pure MgO consists of three bands with maxima 250, 357 and 570 nm, associated with radiation defects [10–14].

Fig. 1 gives the absorption spectra of pure MgO (curves 4–6) and $Ni_cMg_{1-c}O$ single crystals (curves 1–3) before and after fast neutron irradiation.

In addition to the radiation defect bands the small content ($c\leqslant10$ mass%) of nickel impurity in octahedral sites rises absorption bands due to the spin-allowed transitions from the ground state $^3A_{2g}(^3F)$ to the exited states $^3T_{2g}(^3F)$, $^3T_{1g}(^3F)$ and $^3T_{1g}(^3P)$ with maxima at 1200, 650 and 400 nm [15]. The optical absorption spectra of $Ni_{0.5}Mg_{0.5}O$ measured at liquid nitrogen temperature before and after neutron irradiation are shown in Fig. 2. The neutron irradiation of $Ni_cMg_{1-c}O$ single crystals causes the increase of intensities of bands 380, 460 and 750 nm associated with the spin forbidden transitions $^3A_{2g}(F)\rightarrow{}^1T_{1g}(G)$, $^3A_{2g}(F)\rightarrow{}^1A_{1g}(G)$; $^1T_{2g}(D)$, $^3A_{2g}(F)\rightarrow{}^1E(D)$.

The intensities of the spin forbidden transitions depend on the nickel concentration in MgO and on the fast neutron fluence; besides, they are different for individual transitions.

The intensities of the absorption bands ~357 and ~570 nm observed after fast neutron irradiation differ from those for the single-solid solutions $Mn_cMg_{1-c}O$, $Ni_cMg_{1-c}O$ and the pure MgO. The absorption spectra of the pure and doped crystals after irradiation and annealing are given in Fig 3. The activation energies of the corresponding defects are determined using the isothermal

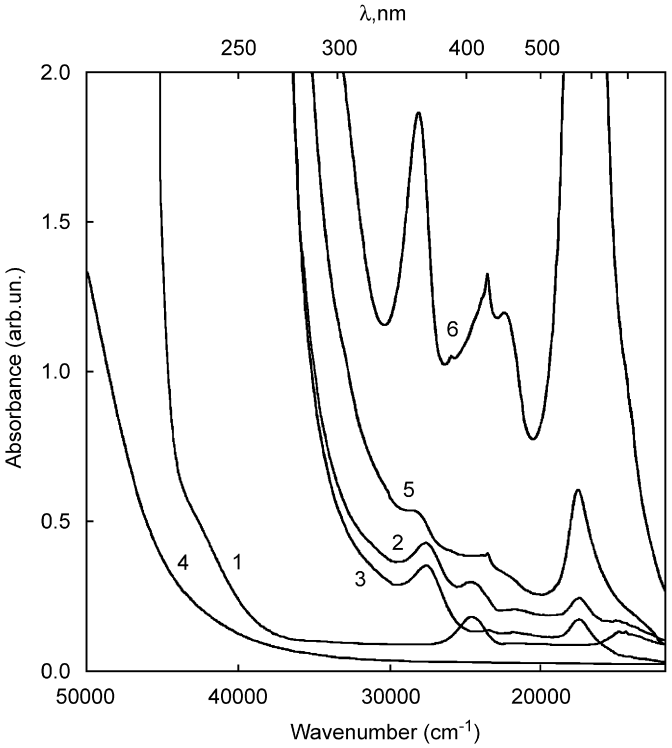

Fig. 1. Optical absorption spectra of MgO:Ni: 1—before irradiation, 2—after fast neutron irradiation $\Phi=10^{16}\,cm^{-2}$, 3—difference (2–1); and of MgO: 4—before irradiation, 5—after fast neutron irradiation $\Phi=10^{16}\,cm^{-2}$, 6—after fast neutron irradiation $\Phi=10^{20}\,cm^{-2}$.

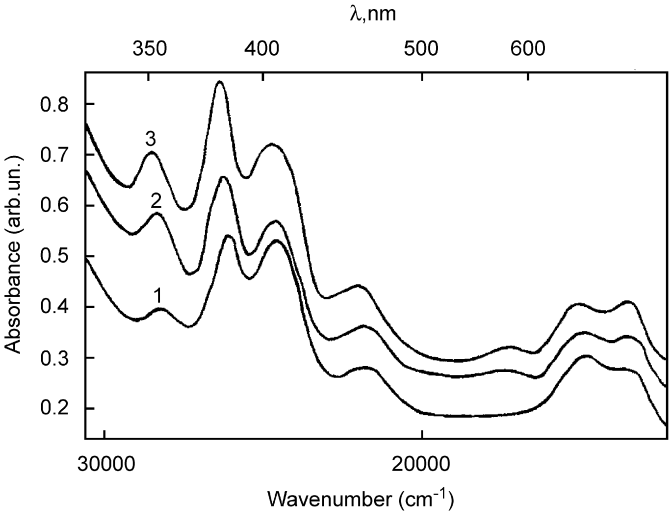

Fig. 2. Optical absorption spectra of $Ni_{0.5}Mg_{0.5}O$ single-solid solution at 80 K: 1—before irradiation, 2—after fast neutron irradiation $\Phi=10^{15}\,cm^{-2}$, 3—after fast neutron irradiation $\Phi=10^{16}\,cm^{-2}$.

annealing data obtained from the intensity behavior of the ~357 and ~570 nm absorption bands during annealing. For the pure magnesium oxide the activation energy is 0.91 and 0.55 eV, for magnesium oxide with nickel impurity −0.71 and 0.81 eV, accordingly. Activation energies smaller than 1.0 eV are typical for the migration processes of interstitial anions and cations [16]. The numerical

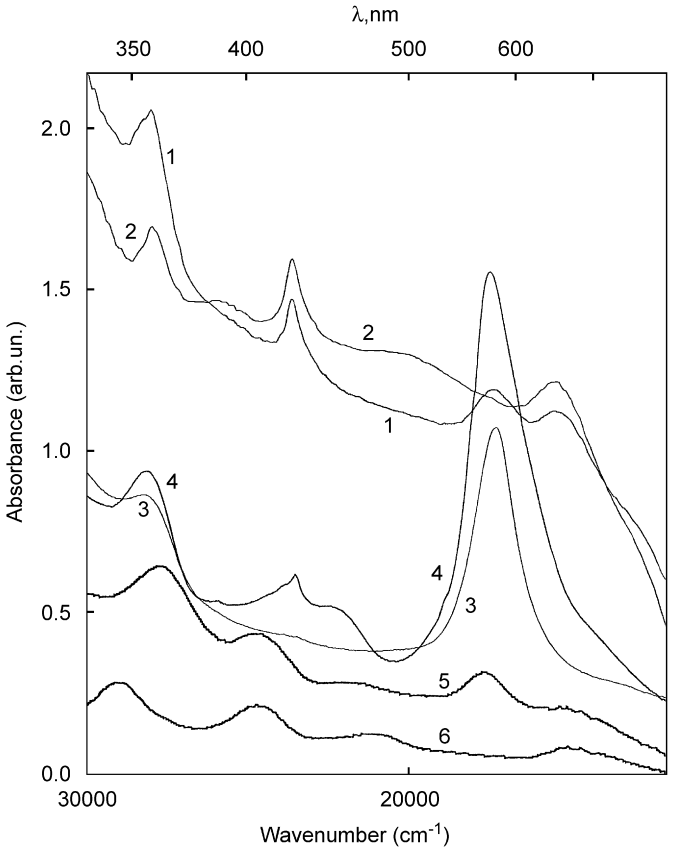

Fig. 3. Optical absorption spectra of crystals irradiated by fast neutrons with fluence $10^{18}\,cm^{-2}$: 1—$Mn_{0.1}Mg_{0.9}O$, 3—MgO, 5—MgO: Ni and annealed for 10 min at temperatures: 2—823 K—$Mn_{0.1}Mg_{0.9}O$, 4—790 K-MgO, 6—878 K—MgO:Ni.

calculation and the experimental data [17,18] show that the activation energies for migration (E_m) of cation and anion vacancies and F^+-, F-centers are very high. In MgO they are $E_m = 2.43$ and 2.50 eV for cation and anion vacancies, respectively; for F^+-centers $E_m = 2.72$ eV; for F-centers $E_m = 3.13$ eV. The migration energies of charged interstitial atoms are much smaller, hence interstitial atoms can migrate even at room temperature. In MgO [18], the activation energies for interstitial anions and cations are $E_m = 0.54$ and $E_m = 0.43$ eV, respectively. These results suggest that the thermal destruction of bands is related to the migration of interstitial anions.

In an irradiation process the impurity ions (nickel, manganese) can form complex centers, which consist of impurity ions and vacancies. In the absorption spectra of $Mn_cMg_{1-c}O$ and $Ni_cMg_{1-c}O$ single-solid solutions the intensity of the ~570 nm band (assigned to the aggregated F- and F^+-centers) is smaller than that in pure MgO. We assume that a part of anion vacancies (F- and F^+-center) is captured by impurity (nickel, manganese) ions forming complexes "Me^{2+}–F^+-center" (Me = Ni, Mn). The exchange interaction in such pairs removes the restriction due to the spin selection rule causing the increase of the intensity of the forbidden transitions. Our investigation shows that at concentrations of impurity ions higher than 10 mass% the probability of formation of aggregate centers (band ~570 nm) consisting of more than three F^+- or F-centers is small.

It is known [14] that in the closed-shell oxides like MgO a hole can change the charge state of one of the neighboring transition metal cations. In MgO a hole can be localized and self-trapped on any of six equivalent O ions—neighbours of an Mg vacancy in MgO, forming an O^- center. A change of the valence state from Me^{2+} to Me^{3+} (Me = Ni, Mn) is possible according to the equation: $Me^{2+} + O^- \rightarrow Me^{3+} + O^{2-}$. An excess charge is compensated by positive ion vacancies. We assume that the 347 and 480 nm absorption bands detected after annealing belong to a complex Ni^{3+}–V_{Mg}. The changes of lattice parameters observed in the irradiated NiO [19] are explained by the creation of Ni^{3+} instead of Ni^{2+}. After neutron irradiation, we also observe a change in the lattice parameters confirming our suggestion.

After thermal treatment of the $Mn_cMg_{1-c}O$ single-solid solution irradiated by fast neutrons, additional wide bands with maxima at 384.6 and 500 nm were observed. The band with a maximum at ~500 nm belongs to a complex Mn^{3+}–V_{Mg}. The spin-allowed transition $^5E \rightarrow {}^5T_2$ of Mn^{3+} was observed in Ref. [20]. The vacancy clusters are theoretically predicted to occur in the transition metal oxides [21–23].

4. Conclusions

It is shown that the fast neutron irradiation leads to the formation of two types complex centers: "Me^{2+}–F^+ (or F) center" and "Me^{3+}–V_{Mg}" (Me = Ni, Mn). The exchange interaction in the pairs "Me^{2+}–F^+ (or F) center" results in the enhancement of the spin forbidden transition intensity in $Me_cMg_{1-c}O$ single-solid solution. The additional bands observed after the thermal treatment of $Me_cMg_{1-c}O$ correspond to the "Me^{3+}–V_{Mg}" complex.

The activation energies of the corresponding defects are determined from the behavior of the ~570 and ~357 nm absorption bands during annealing. The obtained values of activation energy ($E_a < 1$ eV) allow us to assume that the transition ions play an important role in the migration of vacancies and interstitials.

Acknowledgment

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