

Effects of doping with manganese on the optical properties of magnesium aluminate spinel crystals

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The effects of doping with manganese ions on the optical properties of magnesium aluminate spinel crystals grown by Czochralski method were investigated. The optical spectra of the doped crystals have intense absorption in the range of 4.5–6.7 eV which was fit with three absorption bands; the intensity and energy position of these bands vary in dependence on the concentration of doping ions. This effect is explained by formation of F -type centers near the incorporated Mn ions which leads to changes of electronic properties of F^+ -centers and formation of complex defects including Mn-ions. The neutral atmosphere of crystal growth in Czochralski method stimulates the formation of anionic vacancy trapped one electron (F^+ -center). Radio- and photoluminescence spectra demonstrate the bands related to the recombination luminescence at antisite defects, to emission of impurity ions Mn^{2+} and Cr^{3+} -ions, parameters of which indicate the processes of segregation and coagulation antisite defects during the growth of spinel crystals.

Исследовано влияние активации ионами марганца на оптические свойства кристаллов магний-алюминиевой шпинели, выращенных методом Чохральского. Оптические спектры активированных кристаллов содержат интенсивное поглощение в области 4.5–6.7 эВ, которое представляет суперпозицию трёх полос поглощения, интенсивность и спектральное положение которых изменяются в зависимости от концентрации активаторных ионов. Этот эффект объясняется образованием F -типа центров, расположенных вблизи ионов марганца, что приводит к изменению электронных свойств F^+ -центров и образованию комплексов дефектов, включающих ионы марганца. Нейтральная среда выращивания кристаллов по методу Чохральского обуславливает образование анионных вакансий, захвативших один электрон (F^+ -центры). Спектры рентгено- и фотолуминесценции содержат полосы, относящиеся к рекомбинационной люминесценции на дефектах антиструктуры, а также к излучению примесных ионов Mn^{2+} и Cr^{3+} , параметры которых свидетельствуют о наличии процессов сегрегации и коагуляции дефектов антиструктуры в процессе роста кристаллов шпинели.

Magnesium-aluminate spinel crystals ($MgAl_2O_4$) are prospective material for application in science and technology as matrix for fiber-optic temperature sensors, tunable solid state lasers, substrate for microelectronics. Also this spinel is very specific in respect to the crystalline structure due to the existence of the partial inver-

sion, i.e. the cationic disorder which leads to the formation of high-concentration of charged defects $(Mg^{2+}_{octa})^-$ and $(Al^{3+}_{tetra})^+$, so-called antisite defects. The degree of inversion of natural spinel crystals is low but artificially grown crystals have up to 30 % of disordered cations. Because the natural spinel crystals contain the large concentra-

tion of impurity ions such as Cr, Mn, and Fe, this will be one of the reasons for formation of ordered spinel structure. The presence of transition metal impurities in oxide crystals affects quite markedly the optical, electrical, and mechanical properties. The effect is strongly dependent on the valence, aggregation state, and concentration of the impurity.

Incorporation of aliovalent impurities in nominally pure or doped oxide crystals causes the appearance of charge compensating "free" and "bond" defects and formation of the charged or neutral defect clusters. In sapphire crystals doped with magnesium $\text{Al}_2\text{O}_3:\text{Mg}$ the F_{Mg}^- centers are formed which represents the F^+ -centers near Mg^{2+} -ions [1]. In chromium doped $\text{MgO}:\text{Cr}$ the Cr^{3+} centers with Mg vacancies (V_{Mg}) on nearest-neighbor and on the next-nearest-neighbor lattice sites have been identified [2]. Moreover, the doping of CaO with Mg^{2+} isovalent ions leads to the formation of F^- and F^+ -centers at regular anion vacancies along with F_{A}^- and F_{A}^+ -centers on anionic vacancies for which the nearest Ca^{2+} is replaced with Mg^{2+} . There is some evidence for spatial correlated F^- and F_{A}^- -centers [3]. Therefore by variation of aliovalent or isovalent impurity concentration we can manipulate the physical properties which are related to point defects in undoped and impurity-doped crystals. In this paper we investigated the optical properties of magnesium aluminate spinel crystals grown by Czochralski methods and doped with manganese to different concentrations.

We investigated stoichiometric spinel crystals MgAl_2O_4 grown by Czochralski method in argon atmosphere from spinel powder MgAl_2O_4 as nominally pure and doped with Mn to concentration of 0.1 mass.%. Samples with dimensions of $10 \times 10 \text{ mm}^2$ and 0.7 mm thickness were cut from single crystals and polished on both sides to an optical finish. Optical absorption

was measured in the range 1.2–6.4 eV using either a single or dual beam spectrophotometer. Irradiation was performed using a Cu X-ray tube operating at 40 kV and 10 mA. For ultraviolet (UV) irradiation there were used either mercury 600 W lamp or deuterium 400 W lamp, both with quartz tubes. During irradiation the samples were cooled with powerful fan to keep its temperature below 30°C. Radioluminescence (RL) was excited using standard X-ray tube with Cu anode operated at 45 kV and 0.3 mA. Light emission was dispersed with MDR-1 grating monochromator and recorded in the range 1.55–6.2 eV using FEU-106 photomultiplier. Spectral resolution was 1.6 nm in the range 200–400 nm and 3.2 nm in 400–800 nm. Photoluminescence (PL) measurements were provided at the room temperature by using two monochromators: one — for excitation (MDR-12), another — for registration of emission (MDR-1). All spectra were corrected on photomultiplier spectral sensitivity function. Before each measurement of RL and PL the samples were annealed at 650°C during 0.5 h. X-ray diffraction analysis of crystal composition shows only spinel phase of the same lattice parameter independently on the Mn-concentration (Table).

Optical absorption spectra of nominally pure crystals contain wide almost continuous absorption from ~4.5 to 6.6 eV, the intensity (Fig. 1) with some indication on two bands at ~4.8 and ~5.4 eV. The experimental spectra could be fit with three bands of the Gaussian form at 4.8, 5.4, and 6.77 eV. Doping with Mn-ions leads to the changes of the form of absorption spectra, but still all spectra could be fit with three bands the energy positions and intensities of which depend on the concentration of manganese. The first of the indicated bands at 4.8 eV is characteristic for absorption of F^+ -centers (anionic vacancy captured one electron) in stoichiometric spinel crystals [4], but the position of this band shifts to higher energy

Table. Variation of lattice parameter in spinel crystals grown by Czochralski method and doped with manganese to different concentrations

| Concentrat. of Mn | Orientation | Angle of deviation | $a, \text{Å}$ | |
|-------------------|-------------|--------------------|---------------|--------|
| | | | Center | Edge |
| Nominally pure | [310] | 3.8° | 8.0845 | 8.0848 |
| 0.02 mass.% | [310] | 4° | 8.0845 | 8.0842 |
| 0.04 mass.% | [310] | 1.3° | 8.0848 | 8.0842 |
| 0.1 mass.% | [100] | 4° | 8.0838 | 8.0858 |

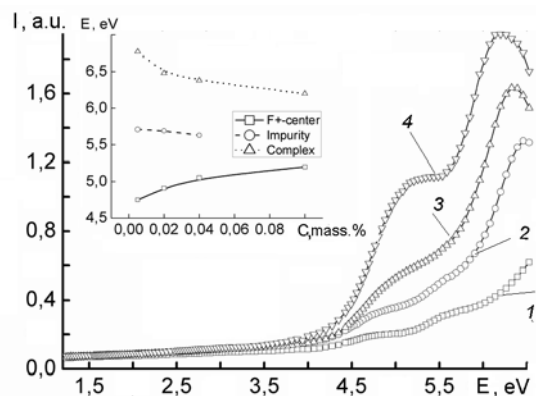


Fig. 1. Absorption spectra of $\text{MgAl}_2\text{O}_4:\text{Mn}$ spinel crystals grown by Czochralski method. The inset plot shows the dependences of energy position of absorption bands on the concentration of Mn-ions in crystals. 1(\square) — nom pure; 2(\circ), 3(Δ), 4(∇) — 0.02, 0.04, 0.1 % Mn.

at the increasing of manganese concentration. The definite interpretation of this band is difficult because at this energy could be situated also the F^+ -band in $\alpha\text{-Al}_2\text{O}_3$ and/or absorption band related to charge transfer transition in Fe^{3+} ions in oxide crystals. Absorption related to charge transfer transitions in Fe^{3+} ions in spinel consist of two bands at 4.75 and 6.4 eV which allow us to conclude on the improbability of this identification, because the second band is absent. The F^+ -centers in $\alpha\text{-Al}_2\text{O}_3$ show also two absorption bands at 4.83 and 5.45 eV [5] which is very close to experimental bands. Nevertheless, the behavior of these two bands with manganese concentration excludes also this identification because the position and intensity of 5.4 eV band do not depend on the Mn-ion content, but the intensity of band at 4.8 eV grows linearly with Mn concentration and its position shifts to higher energy up to 5.2 eV.

The energy position of the last absorption band changes with Mn-concentration in opposite direction from 6.77 eV for nominally pure crystals to 6.4 eV in spinel crystals containing 0.1 mass.% of manganese, the intensity of this band increases also but it tends to saturation at high concentration. In the crystals doped with the highest Mn concentration the experimental spectra could be fit only with two bands at energies of 5.4 and 6.2 eV.

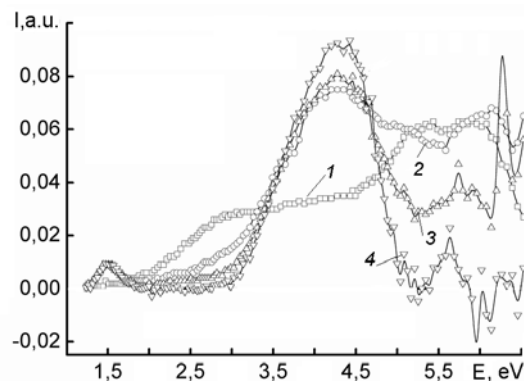


Fig. 2. Difference absorption spectra of MgAl_2O_4 spinel crystals doped with manganese to different concentration and irradiated with UV-light: 1(\square) — nom pure; 2(\circ), 3(Δ), 4(∇) — 0.02, 0.04, 0.1 % Mn.

Therefore, we have concluded that maximum absorption at 4.8 eV is superposition of two bands one of which is caused by F^+ -centers in the presence of some amount of $\alpha\text{-Al}_2\text{O}_3$ phase and another one is related to F^+ -centers situated near Mn-ions in spinel lattice. The formation of F -type centers related to anionic vacancies in the Czochralski grown crystals is consequence of reducing growth atmosphere. The energy position of the third band and its dependence on manganese concentration allow to ascribe it tentatively to complex defects which include lattice defects and impurity ions.

Usually isolated anionic and cationic vacancies in as-grown crystals are optically inactive, but irradiation with UV-light or X-rays leads to charge exchange between defects and impurities and formation of hole centers at cationic vacancies and F -type centers at anionic vacancies. The difference spectra of irradiated and non-irradiated spinel samples doped with manganese to different concentrations are shown in Fig. 2. Irradiation of nominally pure spinel crystals with UV-light demonstrate the prominent radiation-induced absorption bands at 3.1, 4.75, and 5.35 eV which were identified with isolated hole and electron centers. Also there is strong absorption in the vicinity of ~ 4 eV, and the deconvolution of absorption spectra in Gaussians bands gives additional bands at 3.78 and 4.15 eV, which were identified with hole and electron centers at antisite defects [4]:

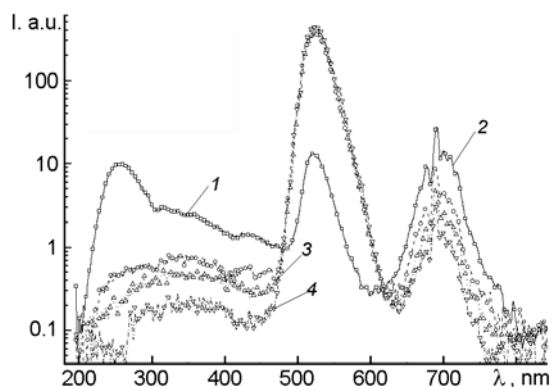
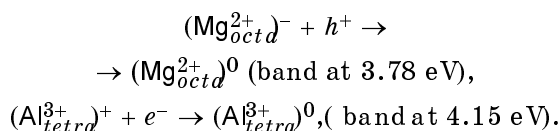


Fig. 3. Radioluminescence spectra of $\text{MgAl}_2\text{O}_4:\text{Mn}$ spinel crystals doped with manganese to different concentrations: 1(\square) — nom pure; 2(\circ), 3(Δ), 4(∇) — 0.02, 0.04, 0.1 % Mn.



Doping with manganese to concentration of 0.02 % leads to disappearance of hole centers at isolated cationic vacancies (the 3.1 eV band), growth of bands at 3.78 and 4.15 eV, at the constant intensity of bands related to F -type centers. In crystals doped with manganese to concentration of 0.04 % and higher there were observed only the bands at 3.78 and 4.15 eV. The previous investigations of kinetics of accumulation and decay of these bands allow us to identify the spatially correlated antisite defects which are responsible for high resistance of this material to displacive irradiation [5]. At the doping with manganese there appear also band at 1.5 eV the origin of which is need to be studied. Therefore, the doping with manganese leads to formation of antisite defects, which are optically active after UV-irradiation and to disappearance of isolated cationic and anionic vacancies.

The existence of defects and impurities could be studied by radioluminescence — the emission which arises under X-ray or gamma-irradiation. At such types of irradiation we generate the free electrons and holes which could be captured by defects and impurity ions with subsequent emission of characteristic photons allowing to identify the nature of emitting species and defects. Because of the detection level of luminescence methods is several orders of magnitude higher to compare with that of absorption it allows to study the defects

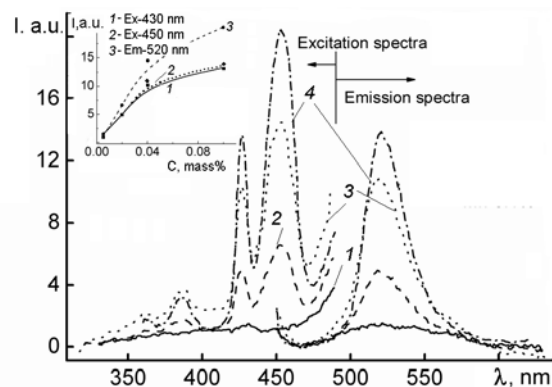


Fig. 4. Excitation/emission spectra of Mn^{2+} -ions in Mn-doped spinel crystals: 1 — nom pure; 2, 3, 4 — 0.02, 0.04, 0.1 % Mn. The inset plot shows the dependencies of intensity of excitation and luminescence bands on the concentration of Mn-ions in $\text{MgAl}_2\text{O}_4:\text{Mn}$ crystals.

and impurity ions at the much lower concentrations. The RL spectra of nominally pure spinel crystals disclose the prominent emission bands at 4.8 (258 nm), 2.38 (520 nm), and 1.8 eV (688.5 nm) which are related to recombination luminescence at antisite defects, to radiative transitions in Mn^{2+} - and Cr^{3+} -ions in spinel crystals, respectively (Fig. 3). For the first time the Mn-doped to 0.01 mol% spinel crystals was studied in cathode-luminescence method [7]. The dependence of luminescence properties of Mn^{2+} -ions on the ordering of spinel lattice was shown in [8]. Our experiment demonstrates that doping with Mn-ions leads to the vanishing of the 4.8 eV band and the decreasing of Cr^{3+} -ions luminescence at the growth of Mn^{2+} -ion band. Because of the UV-emission band is identified with the recombination luminescence this means that some type of antisite defects disappear in Mn-doped spinel crystals.

Magnesium aluminate spinel lattice contains two types of polyhedron formed by oxygen ions: tetrahedral and octahedral sites. Because the energy of preference of Mn^{2+} -ion for octahedral position is equal to zero, they can occupy both positions. The observed luminescence spectra of manganese doped spinel crystals contain the band at 520 nm, which is usually assigned to transitions between the spin-orbit components of the 4T_1 excited state and the 6A_1 ground state of Mn^{2+} in tetrahedral position. The measured excitation spectra of the Mn^{2+} emission are shown in Fig. 4. According to the Tanabe-Sugano scheme the bands at

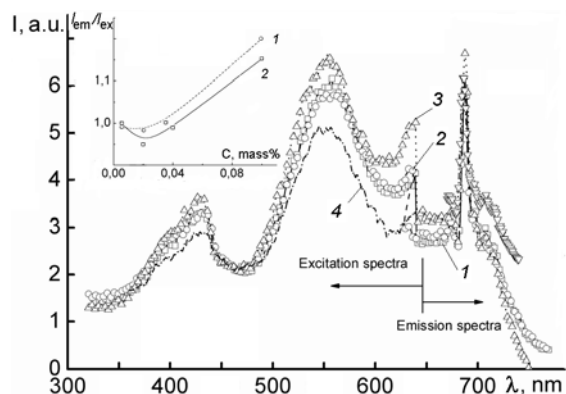


Fig. 5. Excitation/emission spectra of Cr^{3+} in Mn-doped spinel crystals: 1(\square) — nom pure; 2(\circ), 3(Δ), 4(—) — 0.02, 0.04, 0.1 % Mn. The inset plot shows the dependencies of ratio of intensity of excitation to luminescence bands on the concentration of Mn-ions in $\text{MgAl}_2\text{O}_4:\text{Mn}$ crystals (1 — $\lambda_{ex} = 560$ nm. 2 — $\lambda_{ex} = 430$ nm).

460, 430, 390 and 360 nm could be identified with transitions from the ground state ${}^6A_1({}^6S)$ to the ${}^4T_2({}^4G)$, ${}^4A_1({}^4G) + ({}^4E)$, ${}^4T_2({}^4D)$, and ${}^4E({}^4D)$ of Mn^{2+} -ions in tetrahedral position, respectively. Therefore, both the luminescence and excitation spectra confirmed the tetrahedral coordination of Mn^{2+} -ions in spinel lattice, and the large widths of these bands indicate the existence of disordering of occupied sites. Taking into account optical absorption spectra, one can propose that Mn^{2+} ions are surrounded by anionic vacancies and antisite defects in the second and higher coordination spheres. The concentration dependences of intensity of excitation and emission bands are shown in the insert of Fig. 4. In general, the behavior of these bands is correlated to concentration dependence of absorption band at 6.4 eV.

Despite of the doping spinel crystals with manganese, the luminescence of uncontrolled impurities of Cr^{3+} ions could be observed also. The experimental spectra of emission and excitation of Cr^{3+} ions in spinel crystals is shown in Fig. 5. Zero-phonon emission line at wavelength of 688.5 eV originated from the spin-forbidden transition ${}^2E_g \rightarrow {}^4A_{2g}$ in octahedrally coordinated Cr^{3+} (so-called *R*-line). Excitation spectra consist of two bands at 560 and 430 nm related to transitions from ground state to ${}^4T_{2g}$, and ${}^4T_{1g}$, respectively. The position of Cr^{3+} -emission line certainly indicates the octahedral coordination of this ion in spinel lattice, but doublet character of excitation

bands related to field-dependent transitions could be explained by localization of defects (including antisite defects) near incorporated Cr^{3+} -ions. In opposite to Mn^{2+} -ions the efficiency of excitation in both bands is the same, but increasing of manganese concentration to 0.1 mass.% leads to decrease of emission intensity of Cr^{3+} -ions, maybe, because of excitation energy transfer from Cr^{3+} to Mn^{2+} -ions.

It is usually recognized that incorporation in ionic crystals of aliovalent ion as impurity leads to creation of attendant defects for charge compensation. Also incorporation even isovalent ions could create complex defects consisted of impurity and lattice defects, like $\text{Mn}^{2+}-V_O$ in MgO and CaO crystals [9]. Because Mn^{2+} can be placed in tetrahedral and octahedral positions we can expect formation of such complex defects in spinel lattice. Moreover, the inconsistency of size, charge, and electronic structure of impurity ion to the replaced one leads to distortion of regular lattice, which act as attractive or repulsive center for different types of defects including charged antisite defects [10]. Cationic disorder in spinel by itself leads to creation perturbed of Cr^{3+} and Mn^{2+} ions [8]. Irradiation of nominally pure spinel crystals with UV-light or X-rays leads to formation of *V*- and *F*-types centers along with hole and electron centers at antisite defects [4]. Doping with manganese ions causes damping the formation of *V*- and *F*-types centers and enhances the optical centers formation at antisite defects (Fig. 2). There is a correlation between efficiency of RL of Mn-ions and irradiation induced optical center formation at antisite defects in dependence on manganese concentration. This means that incorporated manganese ions serve as centers of segregation and coagulation of antisite defects, some of them is forming absorption centers, others — centers of luminescence. The absence of recombination luminescence in UV range for doped crystals related to antisite defects indicates the vanishing of isolated antisite defects.

In conclusions, the experimental study of the optical properties of manganese doped spinel crystals shows the existence of absorption bands which were identified with *F*⁺-centers distorted by impurity ions. The neutral atmosphere of crystal growth in Czochralski method stimulates the formation of anionic vacancy trapped one electron (*F*⁺-center). The variation of transition energy in these centers from 4.8 eV in nomi-

nally pure crystals to 5.2 eV in crystals doped with manganese to concentration of 0.1 mass.% can be explained by the defective nature of the first and second coordination spheres at localization of Mn-ions near anionic vacancy captured one electron forming F^+ -center. The luminescence of these Mn^{2+} -ions gives the main contribution in RL spectra of spinel crystals. The disappearance of the UV-band related recombination luminescence in manganese doped spinel crystals indicates that Mn-ions also serves as centers of attraction of antisite defects responsible for this emission.

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Вплив активації марганцем на оптичні властивості кристалів магній-алюмінієвої шпінелі

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Досліджено вплив активації іонами марганцю на оптичні властивості кристалів магній-алюмінієвої шпінелі, вирощених методом Чохральського. Оптичні спектри активованих кристалів містять інтенсивне поглинання в області 4.5–6.7 eV, яке є суперпозицією трьох смуг поглинання, інтенсивність та спектральне положення яких змінюються в залежності від концентрації активаторних іонів. Цей ефект пояснюється створенням F -типу центрів, розташованих поблизу іонів марганцю, що призводить до зміни електронних властивостей F^+ -центрів та створення комплексів дефектів до яких входять іони марганцю. Нейтральне середовище вирощування кристалів за методом Чохральського зумовлює створення аніонних вакансій, які захоплюють один електрон (F^+ -центри). Спектри рентгено- та фотолюмінесценції містять смуги, які відносяться до рекомбінаційної люмінесценції на дефектах антиструктури, випромінювання домішкових іонів Mn^{2+} та Cr^{3+} , параметри яких вказують на наявність процесів сегрегації та коагуляції дефектів антиструктури у процесі росту кристалів шпінелі.