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ROLE OF 3d-IONS FOR RADIATION DEFECT

PRODUCTION IN MgO AND MgAl₂O₄

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AND $MgAl_2O_4$

P r e p r i n t

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РОЛЬ ЗАГРЯЗНОВ В ОБРАЗОВАНИИ ДЕФЕКТОВ В MgO И $MgAl_2O_4$

Н.А.Миронова, Г.А.Гринвальд, В.Н.Скворцова

А Б С Т Р А К Т

Рассмотрено влияние по возможности всех видов излучения на оптические свойства кристаллов MgO и $MgAl_2O_4$, содержащих примесные ионы хрома и марганца. Основное внимание уделено сложным дефектам типа "примесь-собственный дефект матрицы". Показано, что в $MgO:Cr^{3+}$ ионы хрома, образующие центры различной симметрии, меняют под внешним воздействием свое валентное состояние с различной эффективностью. Кроме того, можно утверждать, что компенсирующая вакансия не участвует в образовании дырочных центров. В многокристаллах $MgO \cdot Al_2O_3$ присутствие ионов марганца в октаэдрической координации подавляет создание дырочных центров при γ -облучении. При исследовании спектров люминесценции ионов Cr^{3+} в $MgAl_2O_4$ установлено, что облучение нейтронами увеличивает степень инверсии магний-алюминиевой шпинели.

ROLE OF 3d IONS FOR RADIATION DEFECT PRODUCTION IN MgO
AND $MgAl_2O_4$

N.A.Mironova, G.A.Grinvald, V.N.Skvortsova

A B S T R A C T

Optical properties of MgO and $MgAl_2O_4$ crystals containing chromium and manganese impurity ions were studied by exposure to but all types of radiation. Complicated defects of the "impurity-matrix defect" type were preferably considered. It has been shown that different symmetry center forming chromium ions in $MgO:Cr^{3+}$ change their valency with various efficiency being exposed to external action. Besides, the compensating vacancy does not participate in the hole centers formation. For $MgO \cdot Al_2O_3$ single crystals the presence of octahedrally coordinated manganese ions suppresses the hole center creation by γ -irradiation. Studying luminescence spectra of Cr^{3+} ions in $MgAl_2O_4$ it has been stated that neutron irradiation increases the degree of inversion for the manganese-aluminum spinel.

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ROLE OF PA-IONS FOR RADIATION DEFECT PRODUCTION IN
MgO AND $MgAl_2O_4$

Introduction

Studying radiation defect creation investigators have always to take into account the presence of pre-radiation defects in the matrix (impurity ions of transition metals including). In such traditional model systems as MgO , Al_2O_3 , $MgAl_2O_4$ impurity ions of Fe^{2+} , Fe^{3+} , Cr^{3+} , Mn^{2+} usually occur. These ions' optical properties are being studied for a long time, and by now they have been given reliable interpretation basing on the theories of crystal and ligand fields. Contrary to the theory, peculiar nature of transition metal ion spectra manifest itself in the presence of more zero-phonon lines. These additional lines were called "N-lines", and they may be caused by various interactions: e.g. more amount of N-lines in ruby is predetermined by exchange interactions among Cr^{3+} ions [1]; in $MgO:Cr$ they are due to the local symmetry lowering as a result of Cr^{3+} excess charge compensation by neighbouring cation vacancies [2]; in $MgAl_2O_4$ - due to Cr^{3+} local symmetry differences caused by existence of partial inversion in the spinel lattice [3].

Impurity ion and defect interaction could affect ion spectra both qualitatively (N-lines) and quantitatively. It is shown in [4] that for $KMgF_3:Mn^{2+}$, Mn^{2+} ion and F center exchange interaction causes 10^5 times increase in oscillator strength of Mn^{2+} .

The above mentioned point out to the possibility for transition ions to be applied as "monitors" in the crystal self-defect studying, and possible interactions between impurities and matrix self-defects should be taken into account when interpreting the results of radiation effect upon materials.

2. Experimental

Magnesium oxide single crystals were obtained by zone melting. Instrumental neutron activation analysis was applied to determine the impurity ion concentration which was 0.004 mass % for Cr and 0.001 mass % for Mn.

$\text{MgO} \cdot n\text{Al}_2\text{O}_3$ crystals were grown according to the Verneuil method, MnCO_3 salt having been added to the mixture. Manganese concentration measurement method was the same as for magnesium oxide. It gave 10^{-2} and 10^{-3} mass % which was roughly 10 times less than the metal concentration in the mixture. There was 10^{-4} - 10^{-5} mass % of manganese and chromium in nominally pure crystals.

Absorption spectra were measured with the "Specord UV-VIS" spectrophotometer of "Carl Zeiss Iena" production in 200-800 nm range; luminescence spectra - with the SPM-2 monochromator ("Carl Zeiss Iena") having diffraction grating of 651 line/mm. Crystals were excited with the $\Delta\text{KCM}-100$ high pressure xenon lamp having 1000 W capacity and connected to the SPM-1 ("Carl Zeiss Iena") monochromator with the quartz prism. Monitoring was carried out with the $\text{CPD}-119$ photomultiplier tube by synchronic detection method.

EPR spectra were displayed on the P3-1306 radiospectrometer with x-microwave range operation ($f = 9.4$ GHz).

The crystals were irradiated by:

- 1) the YPC-70 X-ray unit with W-X-ray tube ($I = 10$ mA, $V = 35$ kV);
- 2) electrons (3.5 MeV, $I = 0.2$ A/cm²) at doses of 10^{15} - 10^{17} cm⁻² and at 30-60°C ;
- 3) Co^{60} gamma radiation ($E \approx 1.2$ MeV) at doses of 10^2 - 10^5 Gr ;
- 4) neutrons ($E > 0.1$ MeV, 10^{16} - 10^{20} cm⁻² fluence) at $T = 100^\circ\text{C}$ in the IRT reactor (Physics Institute, Latvian SSR Academy of Sciences).

3. $\text{MgO}:\text{Cr}^{3+}$ optical properties

3.1. Spectra identification

Optical and EPR spectra measurements have proved that Mg^{2+} ions are replaced by chromium impurity ions in octahedral lattice sites of MgO . Cr^{3+} ion excess charge is compensated by Mg^{2+} vacancies neighbouring Cr^{3+} [5].

For MgO crystal structure (the rocksalt structure type) there possible two positions of the cation compensating vacancy. The V_{Mg} vacancy placed at [100] direction lowers the crystal field local symmetry from octahedral to tetragonal one, and the same vacancy at [110] direction - to rhombic symmetry.

Chromium centers of various symmetry are presented in Fig.1. Symmetry lowering in the Cr^{3+} ion vicinity results in its energy level splitting. The splitting of 4A_2 ground state has been observed in the EPR spectrum while that of 2E excited state - in the luminescence spectrum of Cr^{3+} ion.

Identification and symmetry of complicated Cr^{3+} centers, as being responsible for $^2E - ^4A_2$ luminescence zero-phonon lines, have been determined according to the line splitting under uniaxial stress [6], luminescence polarisation measurements [7], as well as to the correlation of the line intensity with that of the corresponding EPR spectra [2].

The use of phase-sensitive method of luminescence detection along with absorption polarisation and luminescence measurements have justified [8] that broad-band ($\lambda = 700 \text{ nm} - 1 \mu\text{m}$) luminescence corresponds to rhombic centers (Fig. 1d). It is "fast" ($\tau \approx 35 \text{ ns}$) as compared to that for octahedral and tetragonal centers ($\tau \approx 10 \text{ ns}$) and is related to 4T_2 transition which is by 4A_2 basic level lower for the mentioned centers than 2E level. $^2E - ^4A_2$ luminescence spectra of Cr^{3+} in the zero-phonon region are shown for MgO in Fig. 2. Along with R-line predetermined by single Cr^{3+} ions placed in the octahedral lattice sites, the spectrum evinces some "satellite" lines. The most intensive of them which related to tetragonal centres are indicated by "T"-symbols. The table presents the measured positions of all the luminescence lines and their identification according to the references.

3.2. Effect of ionizing radiation and annealing

Some authors who studied chromium centers in MgO pointed out that various center stability differs. The correlation of different chromium centers' concentration in MgO has been found to considerably change under thermal effect [2,10]. In [10] it is shown that quenching at 1500 K causes high growth of single Cr^{3+} ion concentration (octahedral centers) in relation to tetragonal $\text{Cr}^{3+} - \text{O}^{2-} - V_{\text{Mg}} - \text{O}^{2-} - \text{Cr}^{3+}$ center concentration. It is pointed out in [2] that after annealing at 400°C and slow cooling the intensity of T3 luminescence bands decreases. The changes are more sharp (~ 2 times), if the cooling is rapid. The intensities

of T2 bands change less essentially under the same treatment. That proves lower stability of the T3 center as compared to that of the T2 one.

The present paper have studied X- and γ -radiation effect on Cr^{3+} luminescence spectra for MgO . Fig.3 shows the changes of zero-phonon line intensities as dependent on γ -irradiation dose and the time of exposure to X-rays. Symbols are the same as in Fig.1, and R-line intensity is taken as a unit. On exposure to X-rays the sample was annealed for half an hour at 350°C first, then - at 900°C for the same period of time. After annealing at 900°C the luminescence spectrum reversed to its initial shape. Then the crystal was irradiated by gradually increasing γ -radiation dose.

Both roentgen and gamma radiation affect similarly the luminescence spectrum type. For both the cases the spectra changes indicate a decrease in the concentration of single Cr^{3+} ions, if compared to the concentration of the ions related to V_{Mg} vacancies. It was difficult to determine absolute changes in luminescence intensity for different chromium centers, however, the Cr^{3+} octahedral center concentration seems to decrease under irradiation, and the concentration of tetragonal centers - to grow.

Ionizing radiation cannot create new displaced ions (and, subsequently, new cation vacancies [11]), so the observed changes in various chromium centre concentration should be associated with the changes in Cr^{3+} ion valency states.

Fig.4 presents differentially measured X- and γ -radiation induced absorption spectra.

In the absorption spectrum there appear two intensive bands which should be related to Cr^{2+} (~ 245 nm) and Fe^{3+} (300 nm) ions [12]. Absorption slightly decreases after annealing, and it grows again under γ -irradiation. So, annealing and irradiation alter the chromium ion charge with different efficiency for different chromium centers which is indicated by a change in the correlation of intensities of chromium center luminescence under external action (Figs. 2,3).

Having been exposed to X- and γ -radiation, Cr^{3+} doped MgO absorption spectra do not produce the 540 nm band which is related to color centers; in the EPR spectra hole centers have not been detected as well.

Table

Zero-phonon lines of Cr^{3+} (${}^2\text{E} \rightarrow {}^4\text{A}_2$) luminescence
in MgO at 80 K

(nm)	Identification	Reference source
698.1 (R)	Cr^{3+} octahedral	[2, 6, 7]
698.4 (T3) 702.9 (T3)	$\text{Cr}^{3+}\text{-O}^{2-}\text{-V}_{\text{Mg}}\text{-O}^{2-}\text{-Ga}^{3+}$	[2]
698.8 (T2) 703.5 (T2)	$\left\{ \begin{array}{l} \text{Cr}^{3+}\text{-O}^{2-}\text{-V}_{\text{Mg}}\text{-O}^{2-}\text{-Al}^{3+} \\ \text{Cr}^{3+}\text{-O}^{2-}\text{-V}_{\text{Mg}}\text{-O}^{2-}\text{-Cr}^{3+} \end{array} \right.$	[2] [6, 7]
699.2 (T1') 703.8 (T1)	$\text{Cr}^{3+}\text{-O}^{2-}\text{-V}_{\text{Mg}}$	[6, 7]
(698.1 - 698.7)*	$\text{Cr}^{3+}\text{-O}^{2-}\text{-Cr}^{3+}$	[9]
699.6	} have no reliable identification	
703.1		
704.4		
708.6		

*This center lines were observed for the appointed region
[9] at selected laser excitation.

3.3. Neutron radiation effect

In the optical absorption spectrum under irradiation (Fig. 5) there appear both broad bands which cause blue-violet crystal coloration and a number of sharp peaks. The intensity correlation of sharp (zero-phonon) peaks changes for different crystals; it depends on thermal treatment of a sample.

Two luminescence bands are observed for the neutron irradiated crystals: in the near infrared (IR) (1 - 1.3 μ) and in the red (650 - 850 nm) spectral regions. These bands are of different origin which is indicated by the difference in their excitation spectra: the IR-band has sharp peak in its excitation spectrum at 425 nm, and the red one is excited in a wide region having the maximum at 375 nm. Luminescence of both types is excited in the band at 570 nm.

Fig.6 demonstrates luminescence spectrum for MgO:Cr exposed to $\sim 5 \cdot 10^{18} \text{ cm}^{-2}$ neutronfluence Chromium content in this sample and in those discussed above is the same. For all the studied samples a complicated fine-structure luminescence spectrum is seen to overlap the Cr^{3+} luminescence spectrum.

Two zero-phonon lines at 649 and 642 nm related to various centers have been revealed by absorption investigations in this region [13]. Luminescence studying has detected three more zero-phonon lines at 644.9, 635.6 and 630.6 nm. The intensity correlations for zero-phonon lines are noticeably changed if the excitation wavelength varies (Fig.7). The above allows to associate those lines with various centers. For the irradiated KMgF_3 and KbMgF_3 crystals the bands observed in the mentioned region are associated with the Mn^{2+} -F center complex [4]. Their appearance should be due to the fact that the exchange interaction between radiation induced F centers and Mn^{2+} impurity ions cancels the spin-forbidden electron transitions for Mn^{2+} ions.

For neutron irradiated MgO crystals the luminescence in the red spectral region is possibly related to Mn^{2+} -F (or F^+) center complex.

4. Optical properties of Cr and Mn doped $MgO \cdot n Al_2O_3$ crystals

4.1. Spectra identification

The spinel is referred to the double oxides of the $X^{2+}Y_3^{3+}O_4^{2-}$ -type where X is Mg^{2+} , Ln^{2+} , Fe^{2+} or Mn^{2+} , Y is Al^{3+} , Fe^{3+} , Cr^{3+} three-valence ions. The lattice elementary cell is of cubic symmetry and has eight XY_2O_4 molecules. There are totally 64 tetrahedral and 32 octahedral sites in the spinel structure. In case eight two-valence ions occupy eight tetrahedral sites, and 16 three-valence ones - 16 octahedral sites, the spinel is called "normal", for the "inverse" spinel half of the 3-valence (Y) ions are in tetrahedral positions (A) and the other part of Y-ions and X-ions are usually statistically distributed to octahedral (B) positions.

In spinel crystals transition metal ions should occupy tetra- and/or octa-points that depends on net-stabilization energy [14].

Optical spectra of the magnesium aluminium chromium-doped spinel have been investigated in a number of papers. Both natural [15-17] and synthetic [18-20] crystals were studied. Natural ones with 0.78 weight % of chromium produce two absorption bands: 25800 cm^{-1} and 28520 cm^{-1} which correspond to ${}^4A_{2g}({}^4F) \rightarrow {}^4T_{1g}({}^4F)$ and ${}^4A_{2g}({}^4F) \rightarrow {}^4T_{2g}({}^4F)$ transitions; for some crystals at low temperatures there observed R-lines.

Synthetic spinels have also two wide maximum, characteristic of spin-allowed transitions from the ground level for the Cr^{3+} ion in octahedrally symmetrical field. Some authors [14] detect the band in the 40000 cm^{-1} region.

For magnesium-aluminium chromium doped spinel there observed some zero-phonon lines in the region of Cr^{3+} (${}^2E \rightarrow {}^4A_2$) transition: 1) R-lines predetermined by Cr^{3+} ions which replace Al^{3+} in the octahedral lattice sites of normal spinel [15]; 2) N-lines [3] related to Cr^{3+} ions, local symmetry of which differs from that of the Al^{3+} occupied sites for normal spinels. Basing on the correlation between the line intensities and the crystal thermal treatment, it is shown in [21] that N-line presence is due to inverse distribution of cations in the spinel.

The absorption and luminescence spectra of manganese ions were also studied for natural and synthetic spinels [14,22]. It is shown in [22] that a wide absorption band in the 22700-20000 cm^{-2} region is associated with ${}^5E_g - {}^5T_{2g}$ transition in Mn^{3+} ions, and narrow lines are predetermined by tetrahedrally coordinated Mn^{2+} . All manganese doped spinels produce intense green luminescence. A wide band with the maximum of about 19230 cm^{-1} , characteristic of tetrahedrally coordinated Mn^{2+} , was observed in luminescence spectra. $\text{MgO} \cdot n \text{ Al}_2\text{O}_3$ manganese doped crystals have been spectroscopically investigated in [23].

In MgAl_2O_4 Fe^{2+} are tetrahedrally coordinated [24]; a wide absorption band in the IR region is observed for this compound. At low temperatures the band is resolved into some discrete lines which should be associated to ${}^5E-$ and 5T_2 -state splitting, to simultaneous action of low-symmetry fields and spin-orbital interaction as well as to Jahn-Teller dynamic effect.

Paper [25] gives calculated values of the absorption bands in the visible region related to spin-forbidden electron transitions of tetrahedrally positioned Fe^{2+} .

Further the irradiation effect on the magnesium aluminium spinel is to be discussed.

An effect of ${}^{137}\text{Cs}$ γ -radiation has been studied in [26]. A MgAl_2O_4 crystal was cut from a large cylindrical boule with its axis along the $\langle 100 \rangle$ direction. The crystal contained the following impurities: 76 ppm Fe, 4 ppm Cr, 3 ppm Mn, 22 ppm Cu. There were two absorption bands before irradiation having the maximum at 4.8 and 6.4 eV. The authors relate those bands to octahedrally coordinated Fe^{3+} , as it was done for Al_2O_3 in [27]. After irradiation the bands vanished due to Fe^{3+} charge transfer, and a broad band with the maximum of about 3.1 eV (25001.6 cm^{-1}) was produced. That radiation induced band is strikingly similar to the composite V-type bands near 3.0 eV in Al_2O_3 [28,29] and 2.3 eV in MgO [30], they are associated to O^- - adjacent to a cation site deficient in positive charge. That is why such an origin seems to be possible for the spinel. Gamma radiation produces electrons which are captured at Fe^{3+} in octahedral sites thus producing Fe^{2+} and destroying the 4.8 and 6.4 eV absorption bands.

Similar process occurs in MgO [30].

It has been stated in [31] that bombardment of spinel crystals with 14 MeV neutrons introduces a prominent band at 5.3 eV identified as F-type on the basis of a Mollwo-Ivey-type relationship. The above is justified by the additive coloration [32] which proves that the 5.3 eV band can be initiated by spinel crystals heating in Mg or Al metal vapours, and by heating at the temperature near the melting point in the reducing atmosphere.

For MgAl_2O_4 spinel single crystals the exposure to fast neutrons and accelerated electrons ($E > 0.35$ MeV) introduces an optical absorption band (5 eV) with 1 eV half-width [33]. At the temperature under 40 K that band can be partially "bleached", and a shoulder at 4.75 eV develops concurrently. This bleaching treatment also partially destroys the previously reported V-type absorption centered at 3.2 eV. Further irradiation destroys the 4.75 eV band and restores both the 5.3 and 3.2 eV bands to their original intensities. This process is analogous to the interconversion of F into F^+ centers in Al_2O_3 , so the authors conclude that the 5.3 eV band is the principal optical transition of F-center (two electrons trapped at oxygen-ion vacancy) and the 4.75 eV band is attributed to the absorption by the F^+ center (one electron trapped at an oxygen-ion vacancy).

Experiments on thermal and optical bleaching of the 3 eV absorption complex [34] in crystals with different concentration of Fe^{3+} reveal that this complex is composed of absorption bands located at 2.8, 3.1, 3.6 and possible at 3.9 eV. Analysis of intensity, persistent afterglow and conductivity after γ -irradiation allows to detect a high concentration of shallow electron traps having thermal depth of about 0.9 eV. It is proposed that anti-structure disorder (e.g. Al^{3+} ions in tetrahedral sites) is responsible for a substantial portion of these electron traps.

Gritsina et al. [35,36] have investigated $\text{MgO} \cdot n \text{Al}_2\text{O}_3$ spinel crystals having various mole composition and irradiated by UV-light, X-rays, electron and neutron beams. For $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and $\text{MgO} \cdot 2.5 \text{Al}_2\text{O}_3$ crystals in radiation induced absorption spectra there observed bands in UV-region with the maxima of 235, 260 nm and 230, 255 nm respectively, which are identified by the authors with F and F^+ electron centers. For the irradiated crystals the

visible region of absorption spectra evinces broad overlapping bands identified with transitions in hole centers.

A brief survey allows to summarize : 1) Mn, Cr and Fe ions in spinel crystals have sufficiently been studied; 2) ionizing radiation effect has been investigated for stoichiometric spinel crystals as well as for those manganese- and chromium-unimpured. The aim of this chapter is to observe the 3-d ion role in radiation defect formation.

4.2. Gamma radiation effect upon optical properties of manganese-doped $\text{MgO} \cdot n \text{Al}_2\text{O}_3$

Manganese introduction into the $\text{MgO} \cdot \text{Al}_2\text{O}_3$ stoichiometric spinel causes the appearance of the absorption band in 38000-40000 cm^{-1} region (Figs.8,9; curve 1). The intensity of the band grows under γ -irradiation being considerably more for 0.1 mass % manganese concentration than for that of 0.01 mass %. Besides, in the visible region with the maximum of about 26000 cm^{-1} (385 nm) a broad absorption band appears (Fig.8,9; curves 2,3). For less manganese concentration that band's intensity increases under growing radiation dose, as it is shown in Fig.8 and 9, curves 3.

γ -irradiated $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel having 0.1 mass % manganese concentration produces a new band having not yet reported in literature. Fig. 10 presents the $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Mn}$ 0.1 spinel transmission spectra registered before and after γ -irradiation the dose of 10^5 Gr. Before irradiation a weak band with the maximum of about 5000 cm^{-1} is registered. It slightly increases in intensity under irradiation but further dose growing does not affect it. The new absorption band has the maximum of $\sim 12000 \text{ cm}^{-1}$ (840 nm), its intensity increasing with the dose growth.

A non-stoichiometric magnesium-aluminum spinel ($\text{MgO} \cdot 2\text{Al}_2\text{O}_3$) being doped with manganese ions demonstrates the absorption spectra which are visibly different from those registered for manganese doped stoichiometric spinels. Two bands have been detected : one of them - in the 52000 cm^{-1} region (192.5 nm) and depending significantly on concentration, the other - weak and having the maximum of about 44000 cm^{-1} (225 nm). The absorption spectra are presented in Figs.8,9; curves 4 (the 192.5 nm band is not shown in the figure). The non-stoichiometric spinel with 0.1 mass % manganese concentration being exposed to γ -irradiation produces

a wide band with, supposing, two maxima of 38000 cm^{-1} and 26000 cm^{-1} (Fig.8, curve 5); its intensity increasing with the dose growth (Fig.8, curve 6). For the $\text{MgO} \cdot 2\text{Al}_2\text{O}_3$ spinel with high manganese concentration the changes are not so essential (Fig.9, curves 5,6). For those spinels new bands have not been found in the near IR region.

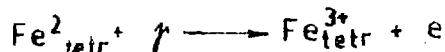
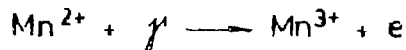
Below we analyse the results obtained.

Since for the crystals under study the absorption bands in the regions of 44000 cm^{-1} (5.4 eV) and 38000 cm^{-1} (4.75 eV) are due to the manganese impurity introduction, they should be related to the absorption bands of octahedrally coordinated Mn^{2+} and to the corresponding transitions from the ground state: ${}^6A_1 \rightarrow {}^4T_2$ (44000 cm^{-1} band) and ${}^6A_1 \rightarrow {}^4A_2$ (38000 cm^{-1} band). Our crystals are also doped with non-monitored quantity of Fe, that is why all the absorption spectra display a weak 5000 cm^{-1} band initiated by tetrahedrally coordinated Fe^{2+} (${}^5E \rightarrow {}^5T_2$ transition) [24].

Now let us discuss the irradiation induced absorption bands.

In all the spectra there is a 26000 cm^{-1} band present, which is the hole center absorption band, and it is identified for sure.

The 38000 cm^{-1} band intensity growth is due to Mn^{3+} or Fe^{3+} concentration increase under irradiation:



Below the absorption band of 12000 cm^{-1} (840 nm) is discussed for the $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Mn}$ spinel. Theoretical analysis has proved [25] the possibility for the band associated with Fe^{2+} in octahedral surrounding to appear in the region of $\sim 10000 \text{ cm}^{-1}$ for the $(\text{MgFe})\text{Al}_2\text{O}_4$ spinel. That band production is principally possible in our case as well, i.e. the released electrons are captured by the present Fe^{3+} in octahedral surrounding, so the latter converts into Fe^{2+} , which is confirmed by the data obtained, since for the case under consideration the 26000 cm^{-1} band increase is not so rapid. But our samples contain a small amount of Fe^{3+} , and taking into consideration that in terms of [37] where the Moessbauer effect was studied, it has been stated that in Fe^{3+} doped MgAl_2O_4 crystals the impurity is distributed equally among tetrahedral and octahedral sites: then we have come to a conclusion that

the novel band should not be related to Fe, but it might be attributed to the Mn^{3+} presence in the octahedral sites.

For γ -irradiated $MgO \cdot Al_2O_3$ single crystals in EPR spectra there appears a signal with $g = 2.014 \pm 0.001$. It was first observed in [38] and associated with the paramagnetic hole center. For $MgAl_2O_4$ we have observed the center intensity to decrease with the manganese concentration increase, the intensity of Mn^{2+} -ion EPR-caused superfine structure lines going down.

Basing on the data obtained we have come to a conclusion that the presence of octahedrally coordinated manganese in $MgO \cdot Al_2O_3$ single crystals suppresses the hole center production under γ -irradiation.

4.3. Radiation effect, upon Cr^{3+} optical spectra for $MgO \cdot n Al_2O_3$

We investigated the chromium doped natural spinel and synthetic $MgO \cdot n Al_2O_3$ crystals with various stoichiometric deviations.

Synthetic crystals differ from natural ones by all zero-phonon line widths and more intensive N-lines as compared to R-lines. The crystal's non-stoichiometry growing, all the zero-phonon line widths and N- and R-line intensity correlations increase (Fig. 11).

Gamma irradiation ($E \approx 1.25$ MeV) by 10^4 Gr dose has not produced any considerable changes in Cr^{3+} luminescence spectra.

Fast neutron irradiation ($E > 1.1$ MeV) by 10^{16} cm^{-2} fluence has caused an absorption band formation with the maximum of 18880 cm^{-1} (535 nm), its intensity grows along with neutron fluence increase. Fig. 12 shows absorption spectra of the chromium doped synthetic $MgO \cdot Al_2O_3$ crystal registered before and after neutron irradiation. The absorption band production is due to Cr^{3+} concentration increase or lowering of its local symmetry.

In luminescence spectra the fluence of 10^{16} cm^{-2} produces an increase in the intensity ratio of N- to R-lines by 5-20 % (Fig. 13). Under the fluence of 10^{20} cm^{-2} the spectrum structure cannot be clearly seen, so the zero-phonon lines are not resolved and Cr^{3+} luminescence integral intensity (${}^2E \rightarrow {}^4A_2$) decreases.

Taking into account that N-line intensities relate to $MgAl_2O_3$ spinel degree of inversion, it is possible to state that neutron irradiation causes an increase in the degree of inversion for the spinels under study.

Conclusion

The presence of transition metal ions in the crystals under consideration influences radiation defect production to a great extent.

It has been stated that for $\text{MgO}:\text{Cr}^{3+}$ ionizing radiation and annealing lead to reversible changes in concentration of different chromium centers. Concentration ratio of Cr^{3+} octahedral and tetrahedral centers reduces under irradiation and grows after annealing. It has been explained by the fact that various symmetry center forming Cr^{3+} ions change their valency with various efficiency being exposed to external action. Besides, the compensating vacancy could not surely take part in the hole center production.

For neutron irradiated MgO the interrelation of radiation induced defects leads to an increase in intercombination transitions for Mn^{2+} -ions.

It has been stated in the paper that for $\text{MgO}\cdot\text{Al}_2\text{O}_3$ single crystals the presence of octahedrally coordinated manganese ions suppresses the hole center production under irradiation. Studying luminescence spectra of Cr^{3+} ions in $\text{MgO}\cdot n\text{Al}_2\text{O}_3$ it has been proved that neutron irradiation causes an increase in the degree of inversion for MgAl_2O_4 .

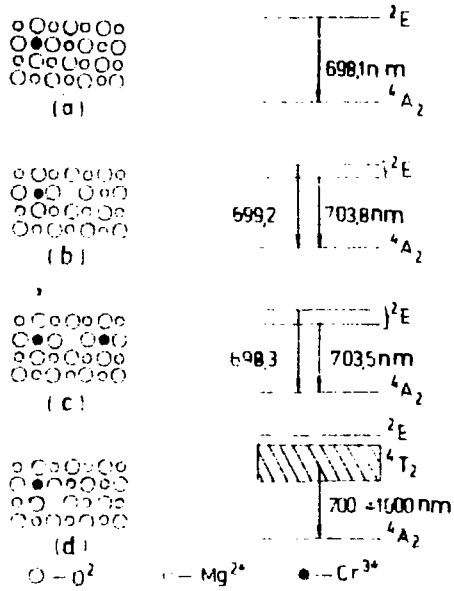


Fig. 1. [7,8]. Representation of the (100) MgO plane containing Cr^{3+} impurity centers in various surroundings: a - an octahedral center; b - a $\text{Cr}^{3+}-\text{V}_{\text{Mg}}$ tetragonal center, [100] direction; c - $\text{Cr}^{3+}-\text{V}_{\text{Mg}}-\text{Cr}^{3+}$ tetragonal center, [100] direction; d - a $\text{Cr}^{3+}-\text{V}_{\text{Mg}}$ rhombic center, [100] direction. On the right there shown their luminescence characteristics.

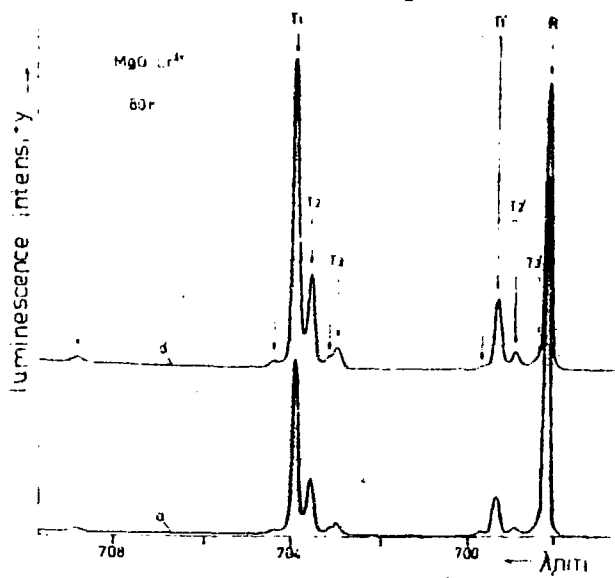


Fig. 2. ${}^2E - 4A_2$ luminescence spectra for $MgO:Cr^{3+}$ in the zero-phonon transition region. Curve a - the initial sample, curve b - after exposure to 8-hour X-radiation.

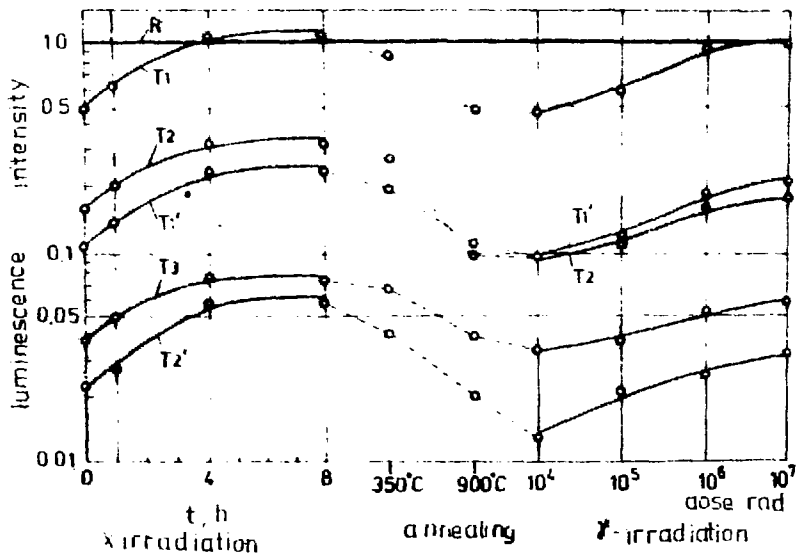


Fig. 3. Relative intensity changes of zero-phonon luminescence lines for $MgO:Cr^{3+}$ at 80 K as depending on irradiation and annealing.

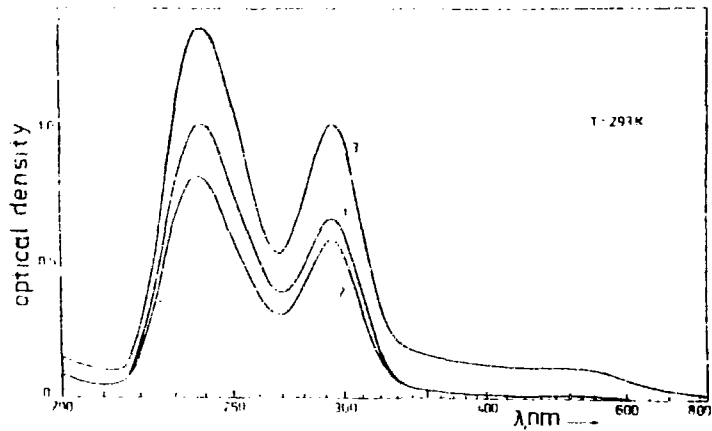


Fig. 4. Spectra of induced absorption for the MgO:Cr crystal differentially measured. 1 - after an exposure to 8-hour X-radiation, 2 - after annealing at 900°C, 3 - after γ -irradiation by 10^4 Gr dose.

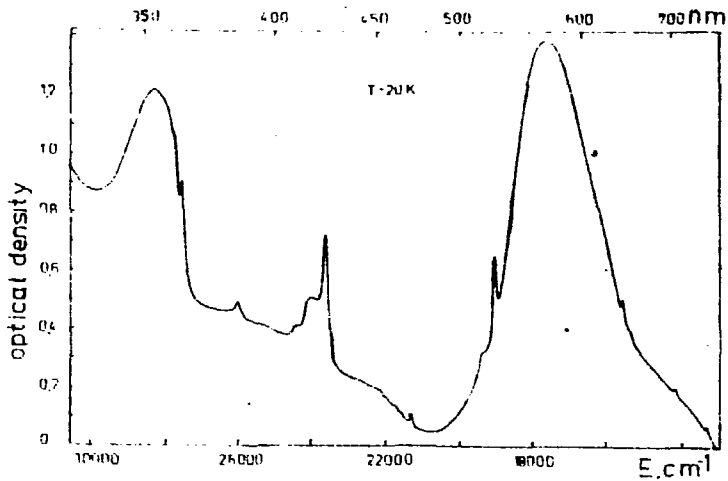


Fig. 5. Absorption spectra of neutron irradiated MgO by the fluence 10^{18} cm^{-2} .

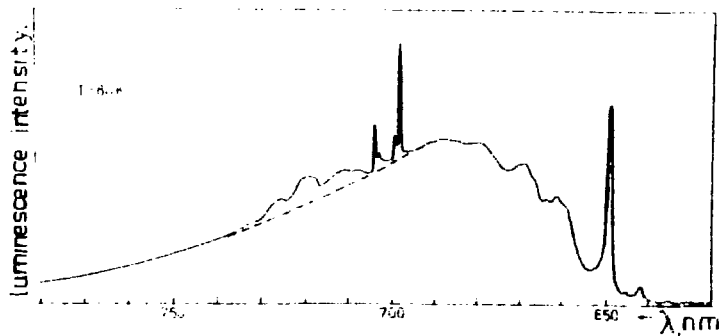


Fig. 6. Luminescence spectra of MgO irradiated by 10^{18} cm^{-2} neutronfluence then annealed at 600°C . Spectral region related to Cr^{3+} impurity ions is above the dashed line.

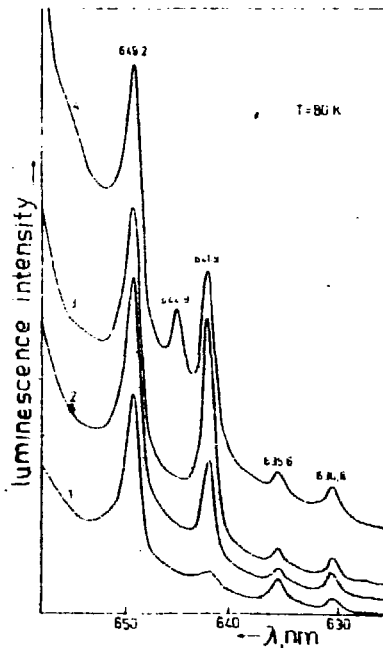


Fig. 7. Long-wave edge of photoluminescence spectra for MgO crystal irradiated by 10^{18} cm^{-2} neutron fluence. Curve 1 - 515 nm wavelength of exciting light, curve 2 - 545 nm, curves 3 and 4 - 565 nm. Curves 1-3 are registered for the crystal annealed at 600°C , curve 4 - for non-annealed one. Spectral width of exciting light gaps is $\sim 20 \text{ nm}$.

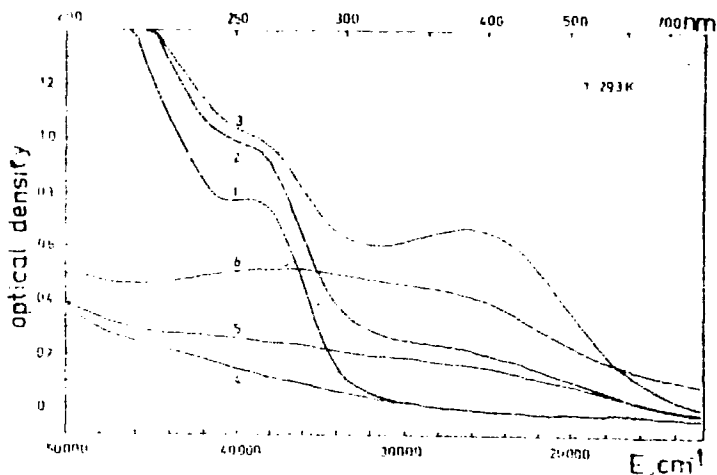


Fig. 8. Absorption spectra for $\text{MgO} \cdot \text{Al}_2\text{O}_3 : \text{Mn}$ 0.01 mass % crystals (1 - before irradiation; 2 - after irradiation by 10^3 Gr γ -irradiation dose; 3 - after irradiation by 10^4 Gr γ -radiation dose) and $\text{MgO} \cdot 2\text{Al}_2\text{O}_3 : \text{Mn}$ 0.01 mass % crystals (4 - before irradiation; 5 - after irradiation by 10^3 Gr γ -radiation dose; 6 - after irradiation by 10^4 Gr γ -radiation dose).

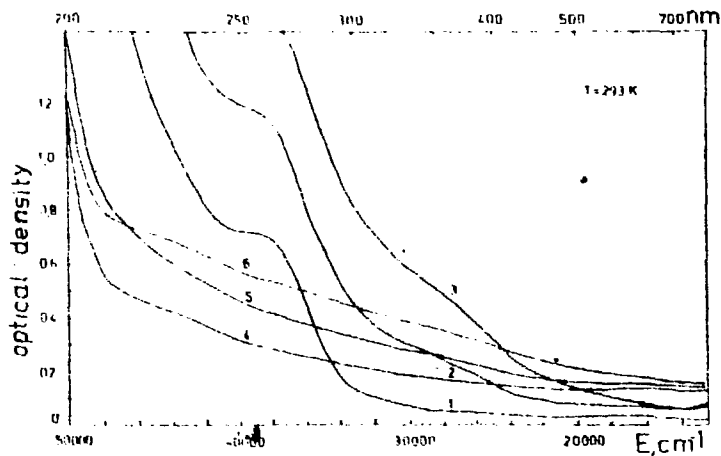


Fig. 9. Absorption spectra for $\text{MgO} \cdot \text{Al}_2\text{O}_3 : \text{Mn}$ 0.1 mass % crystals (1 - before irradiation; 2 - after irradiation by 10^3 Gr γ -radiation dose; 3 - after irradiation by 10^4 Gr γ -radiation dose) and for $\text{MgO} \cdot 2\text{Al}_2\text{O}_3 : \text{Mn}$ 0.1 mass % crystals (4 - before irradiation; 5 - after irradiation by 10^3 Gr γ -radiation dose; 6 - after irradiation by 10^4 Gr γ -radiation dose).

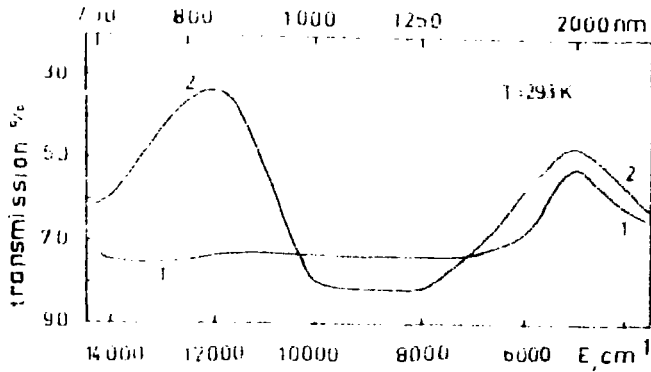


Fig.10. Transmission spectra for the $\text{MgO} \cdot \text{Al}_2\text{O}_3 : \text{Mn}$ 0.1 mass % crystal (1 - before irradiation; 2 - after irradiation by 10^5Gr γ -radiation dose).

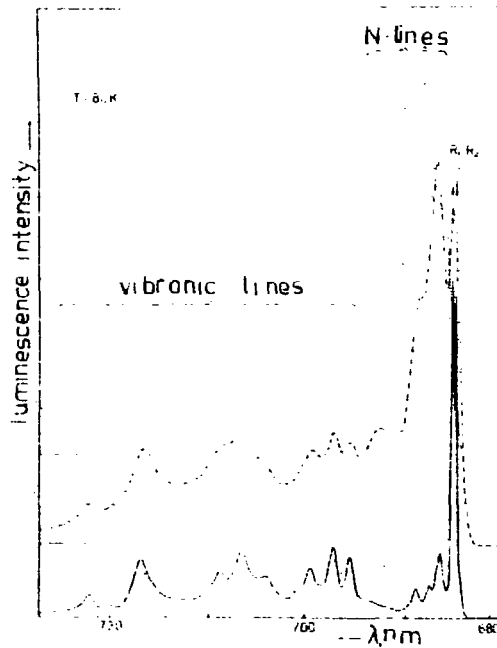


Fig.11. Photoluminescence spectra for magnesium-aluminum Cr^{3+} -doped spinels. Solid line - natural crystal, dashed line - synthetic crystal of $\text{MgO} \cdot \text{Al}_2\text{O}_3$, dotted line - synthetic crystal of $\text{MgO} \cdot 2.5 \text{Al}_2\text{O}_3$.

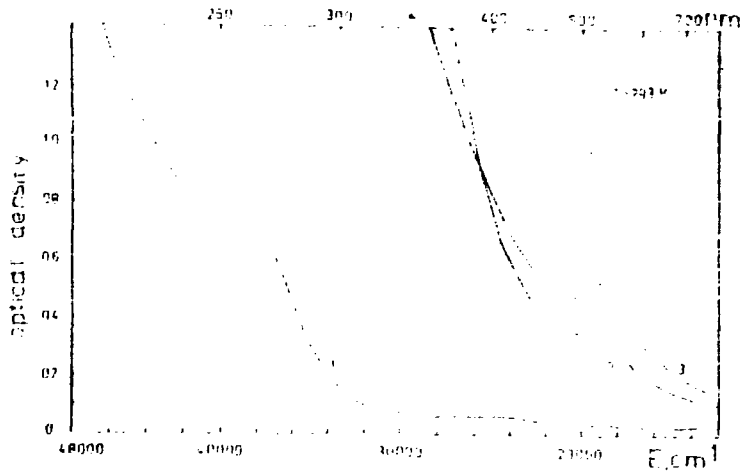


Fig.12. Absorption spectra for the MgO·Al₂O₃:Cr crystal. 1 - before irradiation, 2 - after exposure to 10¹⁶ cm⁻² neutron fluence, 3 - after exposure to 10²⁰ cm⁻² neutron fluence.



Fig.13. Spectra of 4A_2 photoluminescence for the synthetic crystal of MgO·Al₂O₃:Cr³⁺ in the zero-phonon line region. Solid line - before irradiation, dashed line - after irradiation by 10¹⁶ cm⁻² neutron fluence

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РОЛЬ $3d$ ИОНОВ В ОБРАЗОВАНИИ РАДИАЦИОННЫХ ДЕФЕКТОВ
В MgO И $MgAl_2O_4$

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