



## STRUCTURE AND PHASE CHANGES IN NATURAL AND SYNTHETIC MAGNESIUM ALUMINIUM SPINEL

Vera Skvortsova, Nina Mironova-Ulmane, Daina Riekstiņa

Institute of Solid State Physics, University of Latvia

8 Kengaraga St., LV 1063, Riga, Latvia

Fax: + (371)67132778, e-mail: vskv@visiting.lv

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**Abstract.** *Natural spinel crystals from Ural and Pamir deposits and synthetic magnesium aluminium spinel single crystals with different stoichiometry ( $MgO \cdot nAl_2O_3$ ) grown by Verneuil method were used. The photoluminescence (PL), its excitation (PLE) and optical absorption of stoichiometric and nonstoichiometric magnesium aluminium spinel crystals containing the chromium and manganese ions and defects produced by fast neutron irradiation (fluence up to  $10^{20} \text{ cm}^{-2}$ ,  $E > 0.1 \text{ MeV}$ ) are investigated. The broadening of R- and N-lines takes place in synthetic stoichiometric spinel. Structure of synthetic nonstoichiometric spinels ( $n > 1$ ) has to be more disordered, since in addition to the site exchange the so called stoichiometric vacancies are present in the structure. The R- and N-lines broadening takes place after spinel crystals irradiation by fast neutron too. The neutron irradiation causes increasing of the spinel inversion. Furthermore the great deviation from stoichiometry leads to the local structure of  $\alpha\text{-Al}_2\text{O}_3$  formation around  $\text{Cr}^{3+}$  ions. The orange emission band at 570 nm is belonging to complex center " $\text{Mn}^{2+}\text{-F}^+$  (or F centre)".*

**Keywords:** *magnesium aluminium spinel, neutron irradiation, absorption and luminescence spectra.*

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### Introduction

Magnesium aluminium spinel is mixed oxide with high melting temperature at 2135 °C. It has good thermal and mechanical properties, high hardness and low electrical loss.  $MgAl_2O_4$  thin film is a possible candidate for the development of integrated humidity sensors [1]. Spinel single crystals are used for substrate in integrated electronics [2], they are known as laser materials [3-6]. Since magnesium aluminium spinel is highly resistant to neutron irradiation it is considered to be a candidate material for fusion reactor application such as dielectric windows for radio – frequency heating systems and insulators for magnetic coils [7-11]. Oxide spinels have attracted great attention in the field of Earth science because of their importance as constituent minerals in many igneous and metamorphic rocks [12].

The spinel belongs to double oxides of the  $X^{2+}(Y^{3+})_2O_4$  type, where X is  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$  or other bivalent ions, and Y is  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Mn^{3+}$  or other trivalent ions. Magnesium aluminium spinel  $MgO \cdot nAl_2O_3$  (if stoichiometric,  $n=1$ ) is a cubic-type face centred crystal. The elementary cell consists of 8 formula units  $XY_2O_4$ . Oxygen ions create a close-packed arrangement with 64 tetrahedral and 32 octahedral interstices per cell. If eight bivalent ions occupy eight tetrahedral (A) sites, and 16 trivalent ones – 16 octahedral (B) sites, the spinel is described by the space symmetry group  $O_h^7$  and is called "normal". For the "inverse" spinel, a half of the trivalent (Y) ions is located in the tetrahedral position; the other part of Y and X ions is usually statistically distributed between the octahedral positions. If we use an inversion parameter  $i$ , the chemical formula of magnesium aluminium spinel may be expressed by  $^{IV}(Mg_{1-i}Al_i)^{VI}[Mg_{-i}Al_{2-i}]O_4$ , where  $^{IV}()$  and  $^{VI}[]$  represents the tetrahedral (A sites; 8a) and the octahedral sites (B site; 16d). Assuming  $i = 1$ , we obtain a formula  $Al[MgAl]O_4$  for the inverse spinel.

Transition metal ions in magnesium aluminium spinel have been studied extensively, and their optical spectra in the infrared and visible part of a spectra are satisfactorily understood. Nevertheless, there is little information about the influence of fast neutron radiation on impurities behavior. The paper presents investigations of the of the structure and phase changes in natural and synthetic magnesium aluminium spinel crystals containing transition metal ions (Cr, Mn) and irradiated by fast neutron.

### Materials and methods

Natural spinel crystals from Ural and Pamir deposits and synthetic magnesium aluminium spinel single crystals with different stoichiometry ( $\text{MgO}\cdot n\text{Al}_2\text{O}_3$ ) grown by Verneuil method were used. Crystals labelled as 'Mn' have been doped with manganese. Chromium ions are used as a sensitive probe for absorption and luminescence spectra investigation.

Micro (Cr, Mn, Fe) and macrocomponent (Mg, Al) quantities have been detected by the instrumental neutron activation analysis technique [13]. Concentrations of some impurities (mass %) are given in Tab.1. The Tab. 2 presents the results of the determination of the macrocomponents in the magnesium-aluminium spinels. Sample thickness was in the range of 0.5–1 mm.

Table 1.

**The concentration of the impurities in the spinel, mass %**

Notation	Cr	Mn	Fe
Black	$1.5 \times 10^{-3}$	23	1.2
Pink	$2 \times 10^{-3}$	2.9	0.31
Dark pink	$8.0 \times 10^{-2}$	0.1	$3 \times 10^{-2}$
Middle pink	$7.0 \times 10^{-2}$	0.1	$6 \times 10^{-2}$
Lilac	$9.8 \times 10^{-5}$	0.02	1.31
$\text{MgO}\cdot\text{Al}_2\text{O}_3$ (1)	$0.43 \times 10^{-4}$	$0.3 \times 10^{-4}$	$1 \times 10^{-3}$
$\text{MgO}\cdot\text{Al}_2\text{O}_3$ (2)	$0.41 \times 10^{-4}$	$0.16 \times 10^{-4}$	$8.1 \times 10^{-4}$
$\text{MgO}\cdot 2\text{Al}_2\text{O}_3$	$1.25 \times 10^{-4}$	$0.17 \times 10^{-4}$	$4 \times 10^{-4}$
$\text{MgO}\cdot 2.8\text{Al}_2\text{O}_3$	$0.99 \times 10^{-4}$	$0.2 \times 10^{-4}$	----
$\text{MgO}\cdot\text{Al}_2\text{O}_3$ (MA 1:1 Mn 0.1)	$4.3 \times 10^{-4}$	0.015	$1.2 \times 10^{-4}$
$\text{MgO}\cdot 2.5\text{Al}_2\text{O}_3\text{Mn}0.1$	$\leq 1 \times 10^{-4}$	$3.0 \times 10^{-2}$	$1.4 \times 10^{-2}$

Table 2.

**The contents of the macrocomponents of  $\text{MgO}\cdot n\text{Al}_2\text{O}_3$**

Notation	Introduced	Obtained
$\text{MgO}\cdot\text{Al}_2\text{O}_3$ (MA 1:1)	1:1	1:0.9
$\text{MgO}\cdot\text{Al}_2\text{O}_3$ (MA 1:1)	1:1	1:1.5
$\text{MgO}\cdot 2\text{Al}_2\text{O}_3$ (MA 1:2)	1:2	1:1.7
$\text{MgO}\cdot 2.8\text{Al}_2\text{O}_3$ (MA 1:2.8)	1:2.8	1:2.5

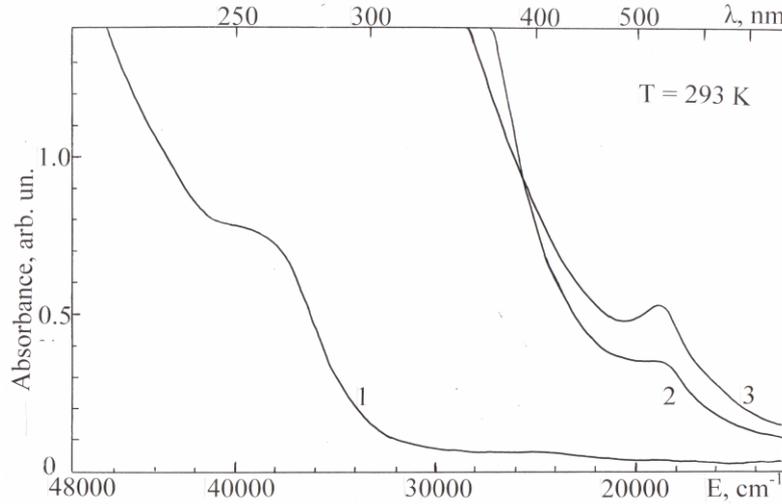
Luminescence spectra of spinel crystals have been measured at liquid nitrogen temperature with an SPM-2 monochromator having a diffraction grating of 651 lines per mm. Crystals were excited by a high pressure xenon lamp (DKSEL-1000) connected to a monochromator (ZMR-1) with a quartz prism. Monitoring was carried out with a photomultiplier tube (FEU-119) using a synchronic detection method.

The neutron irradiation was performed in the Latvian 5MW water-water research reactor. The fluence of fast neutrons with an energy  $> 0.1$  MeV was in the range of  $10^{14}$  -  $10^{20}$   $\text{cm}^{-2}$ . The accompanied  $\gamma$ -irradiation with average energy 1.1 MeV gave an absorption dose of 0.33 Gy. The irradiation temperature was 293 K. A cadmium filter was used for thermal neutron absorption.

The optical absorption spectra were measured with a double-beam spectrophotometer "Specord M-40" (Karl Zeiss Jena) operating in the wavelength region of 200–900 nm ( $50000$ – $11000$   $\text{cm}^{-1}$ ). Optical measurements before and after irradiation were carried out at 293 and 80 K temperature.

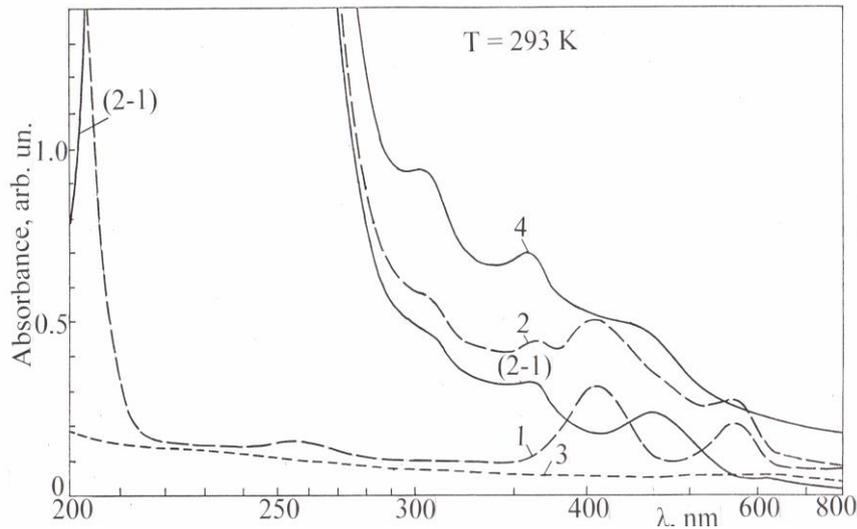
**Results and discussion**

Fig. 1 shows the absorption spectra of MgO·Al<sub>2</sub>O<sub>3</sub> single crystals before and after fast neutron irradiation. After irradiation there appears an intense absorption on the long edge and occurs the characteristic maximum at 535 nm. The intensity of this peak grows with fast neutron fluence increasing.



**Fig.1. Absorption spectra of MgO·Al<sub>2</sub>O<sub>3</sub> single crystals:**  
1. before irradiation, 2. after fast neutron  $\Phi=10^{16}\text{cm}^{-2}$ , 3.  $\Phi=10^{20}\text{cm}^{-2}$

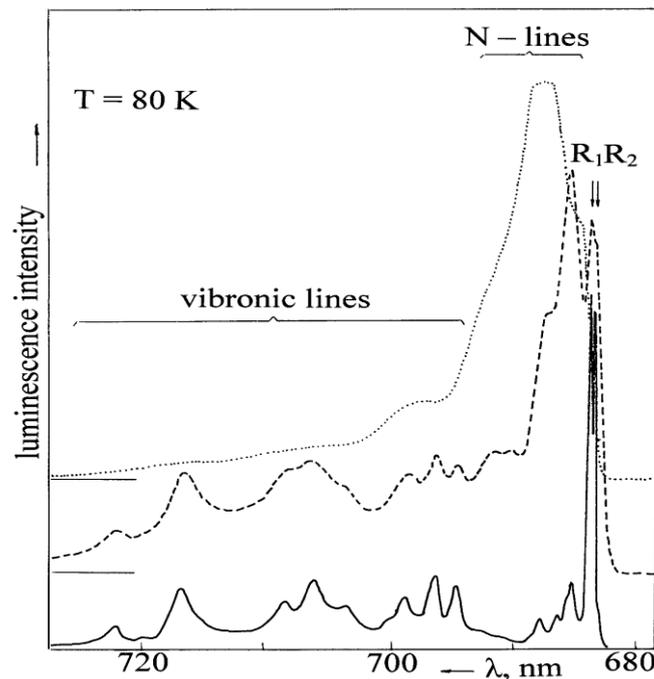
The neutron irradiations of crystal with great deviation from stoichiometry ( $n > 2.5$ ) have just the opposite absorption spectra (Fig. 2). Before irradiation the crystal is transparent. After irradiation at fluence  $\Phi=10^{16}\text{cm}^{-2}$  in absorption spectra there is observed intensive absorption at  $\lambda < 280\text{ nm}$  and bands at maxima 305, 355 and 470 nm. The same effect gives neutron irradiation of the  $\alpha\text{-Al}_2\text{O}_3\text{:Cr}$  crystal. The band's location, which has been produced by neutron irradiation for  $\alpha\text{-Al}_2\text{O}_3\text{:Cr}$  is similar to MgO·2.8Al<sub>2</sub>O<sub>3</sub> (Fig.2, curve 4).



**Fig. 2. Absorption spectra of  $\alpha\text{-Al}_2\text{O}_3\text{:Cr}$ :**  
1. before irradiation, 2. after fast neutron  $\Phi=10^{16}\text{cm}^{-2}$  irradiation, (2-1). additional absorption spectrum, 3. MgO·2.8Al<sub>2</sub>O<sub>3</sub> single crystals before irradiation, 4. after fast neutron  $\Phi=10^{16}\text{cm}^{-2}$

The photoluminescence spectra of natural and synthetic magnesium aluminium crystals with different stoichiometry are given in Fig. 3. In the natural spinel spectra (Fig.3, solid line) some zero-phonon lines were observed in the region of the Cr<sup>3+</sup> ions electron transition

${}^2E_g \rightarrow {}^4A_{2g}$ : R-lines (684.7 and 684.5 nm) predetermined by  $Cr^{3+}$  ions, which replace  $Al^{3+}$  ions in the octahedral sites of the spinel lattice; N-lines (686.0, 688.2, 690.9 and 692.3 nm) related to the  $Cr^{3+}$  ions, which local symmetry differs from symmetry of sites occupied by  $Al^{3+}$  in normal spinel.

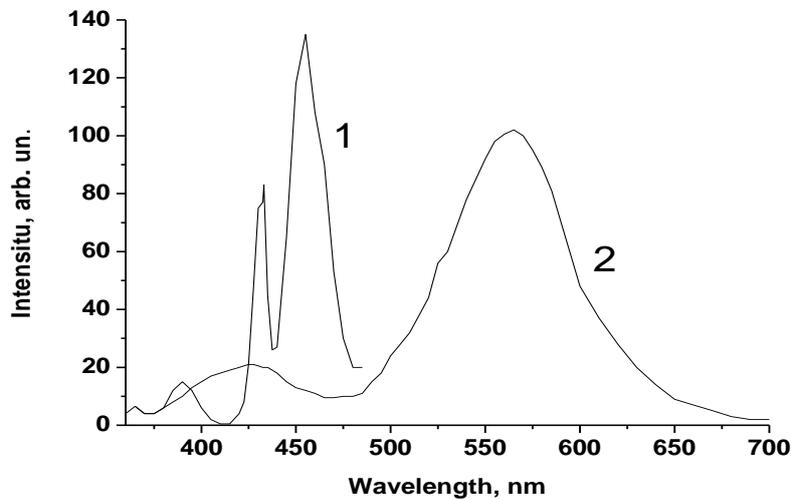


**Fig.3. Photoluminescence spectra of magnesium aluminium spinel.**  
**Solid line – natural spinel, dashed line – synthetic crystal  $MgO \cdot Al_2O_3$ ,**  
**dotted line - synthetic crystal  $MgO \cdot 2.8Al_2O_3$**

The broadening of R- and N-lines takes place in synthetic stoichiometric spinel (Fig. 3, dashed line). Structure of synthetic nonstoichiometric spinels ( $n > 1$ ) has to be more disordered, since in addition to the site exchange the so called stoichiometric vacancies are present in the structure. Therefore, the numbers of different versions of cation location in the 2nd coordination sphere increases. Moreover, an absence of a cation affects  $Cr^{3+}$  ion stronger than  $Mg^{2+}$  substituted for  $Al^{3+}$ . The number of  $Cr^{3+}$  ions with normal arrangement becomes negligible. As a consequence, in the luminescence spectra of a nonstoichiometric spinel one can observe the highly broadened bands with rather intensive N-lines and without signs of R-lines (Fig.3, dotted line). The broadening of R- and N-lines takes place after spinel crystals irradiation with fast neutrons [14]. The photoluminescence spectra of  $MgO \cdot 2.8Al_2O_3$  crystal is shown in Fig.5b. Before irradiation (Fig. 5b, curve 1) spectrum consists of so-called N-lines only [15]. After irradiation by fluence  $\Phi = 10^{16} cm^{-2}$  there appears two broad bands 470 and 580 nm (Fig.5b, curve 2). The  $Cr^{3+}$  luminescence spectrum completely changes (the luminescence spectra are observed at  $\lambda_{ex} = 400$  nm). Luminescence spectra of the irradiated  $MgO \cdot 2.8Al_2O_3$  crystal have been compared to that of  $\alpha-Al_2O_3:Cr$  crystal. Position of the sharp lines of irradiated  $MgO \cdot 2.8Al_2O_3$  crystal coincides with the  $R_1$  and  $R_2$  lines position for  $\alpha-Al_2O_3:Cr$  crystal. Taking into consideration that N – lines intensity is closely associated with the inversion parameter, it is possible to state that neutron irradiation causes increasing of the spinel inversion. Furthermore at high deviation from stoichiometry in magnesium aluminium spinel around the  $Cr^{3+}$  ions the local structure of  $\alpha-Al_2O_3$  is observed.

In absorption spectra of manganese containing nonstoichiometric magnesium-aluminium  $MgO \cdot 2.5Al_2O_3$  spinel, bands at 367, 430, 451, 550 and 610 nm are observed. Stoichiometric  $MgAl_2O_4$  single crystal has the more complex shape. Apart from the above mentioned sharp lines two broad bands with maxima 390 and 555 nm as well as 260 nm band are found out.

For  $Mn^{2+}$  ( $3d^5$ -configuration) the net stabilization energy is zero kkal/mol [16], therefore,  $Mn^{2+}$  ions equally possibly are situated in tetra- or octasites. Figure.4 shows photoluminescence excitation spectra of  $MgO \cdot Al_2O_3 : Mn_{0.1}$  crystal at  $\lambda_{lum} = 520$  nm and  $\lambda_{lum} = 700$  nm.



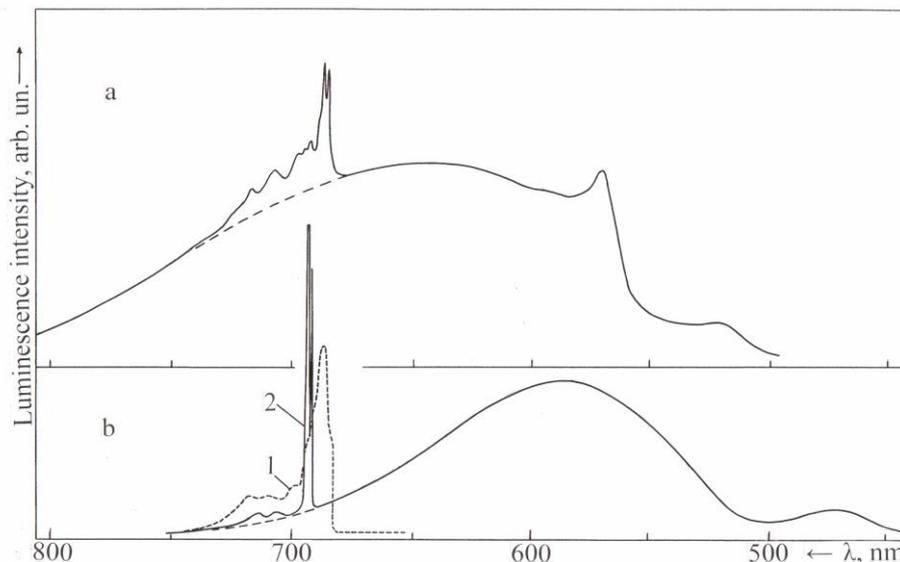
**Fig.4. Photoluminescence excitation spectra of  $MgO \cdot Al_2O_3 : Mn_{0.1}$  crystal:**  
1 -  $\lambda_{lum} = 520$  nm, 2 -  $\lambda_{lum} = 700$  nm

The spectra obtained at 520 nm showed two sharp lines at 433 and 455 nm, but for  $\lambda_{lum} = 700$  nm there are observed two broad lines 565 and 430 nm, which correspond to energies of the  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  and  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  transition of  $Cr^{3+}$  ions. Shapes of the excitation spectra of stoichiometric and nonstoichiometric spinel are identical. But the relationship between band intensity and manganese concentration differs from sample to sample according to its composition. In contrast to synthetic spinel an emission band with a maximum at 625 nm has been found in natural spinel (dark and middle). An emission band with fine structure around 640 nm has been revealed in natural lilac colored spinel in addition to the band at 510 nm [17]. Photoluminescence spectra of  $MgO \cdot Al_2O_3$ : crystal containing 0.1 mass% of manganese is given in Fig.5a. Before irradiation spectra contain only  $Cr^{3+}$  impurity bands. After irradiation there appears a broad emission band, which spreads from 500 to 800 nm ( $\lambda_{ex} = 470$  nm). Band at 520 nm is connected with  $Mn^{2+}$  ions occupying tetrahedral site in spinel structure. Green emission has been observed in synthetic stoichiometric and nonstoichiometric spinel with manganese impurity [18].

After irradiation a band at 570 nm appears in photoluminescence spectra of  $MgO \cdot Al_2O_3$ : crystal containing 0.1 mass% of manganese (Fig. 5a). This band appears only at low temperature in pattern containing manganese. Evidently, that the broad emission line 500-800 nm is connected with intrinsic defects, but peak 570 nm - with complex centers, because it appears after neutron irradiation only in the crystal containing manganese impurity.

A model which explains the observed features is that  $Mn^{2+}$  impurity ions are perturbed by presence of a nearby F or  $F^+$  center (anion vacancies in the spinel can capture one or two electron to form  $F^+$  and F centers [19]). The presence of a nearby F or  $F^+$  center may modify the environment at the  $Mn^{2+}$  impurity site to produce an effective increase in the crystal field. In addition to the shift in energy, the perturbation induced by the F or  $F^+$  center can increase the oscillator strength by introducing odd components to the crystal field, or by exchange coupling between the F or  $F^+$  center and the  $Mn^{2+}$  impurity. The enhancement of the oscillator strength by the exchange interaction has been previously observed between F centers and transition metal impurity ions in  $MgF_2$ ,  $MgAl_2O_4$  and  $MgO$  [20-24]. As the concentration of F and  $F^+$  centers increased, the number of perturbed manganese sites also increased, so that the

excitation peaks became more intense as a function of neutron dose. Since orange emission is attributed to  $Mn^{2+}$  in octahedral coordination, it is possible to assume that the band at 570 nm belongs to a complex center " $Mn^{2+}-F^+$  (or F centre)".



**Fig.5. Photoluminescence spectra of  $MgO \cdot Al_2O_3:Mn_{0.1}$  (a) and  $MgO \cdot 2.8Al_2O_3$  (b) crystal irradiated by fast neutrons.  $T = 80$  K**

### Summary

The photoluminescence (PL), its excitation (PLE) and optical absorption of stoichiometric and nonstoichiometric magnesium aluminium spinel crystals containing chromium and manganese ions and defects produced with fast neutron irradiation fluence up to  $10^{20} cm^{-2}$  ( $E > 0.1$  MeV) are investigated. Natural spinel crystals from Ural and Pamir deposits and synthetic magnesium aluminium spinel single crystals with different stoichiometry ( $MgO_nAl_2O_3$ ) grown by Verneuil method were used. Micro (Cr, Mn, and Fe) and macro component (Mg, Al) quantities have been detected by instrumental neutron activation analysis technique. Chromium ions are used as a sensitive probe for absorption and luminescence spectra investigation.

In the natural spinel spectra some zero-phonon lines were observed in the region of the  $Cr^{3+}$  ions electron transition  ${}^2E_g \rightarrow {}^4A_{2g}$ : R-lines predetermined by  $Cr^{3+}$  ions, which replace  $Al^{3+}$  ions in the octahedral sites of the spinel lattice; N-lines related to the  $Cr^{3+}$  ions the local symmetry, which differs from symmetry of sites occupied by  $Al^{3+}$  in normal spinel. The broadening of R- and N-lines takes place in synthetic stoichiometric spinel. The R- and N-lines broadening takes place after spinel crystals irradiation by fast neutrons, too. Taking into consideration that N – lines' intensity is closely associated with the inversion parameter, it is possible to state that neutron irradiation causes increasing of spinel inversion. Furthermore the great deviation from stoichiometry leads to the local structure of  $\alpha-Al_2O_3$  formation around  $Cr^{3+}$  ions.

The orange emission is attributing to  $Mn^{2+}$  in octahedral coordination, it is possible to assume that the band at 570 nm belongs to a complex center " $Mn^{2+}-F^+$  (or F centre)".

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