ELSEVIER

Nuclear Instruments and Methods in Physics Research B 191 (2002) 256–260

NIM B
Beam Interactions with Materials & Atoms

www.elsevier.com/locate/nimb

Neutron irradiation influence on magnesium aluminium spinel inversion

V. Skvortsova *, N. Mironova-Ulmane, U. Ulmanis

Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street, LV-1063, Riga, Latvia

Abstract

Grown by the Verneuil method $MgO \cdot nAl_2O_3$ single crystals and natural spinel crystal have been studied using X-ray diffraction and photoluminescence spectra. The fast neutron irradiation of magnesium aluminium spinel leads to the lattice parameter decrease. The bond lengths of Mg–O and Al–O vary with the u-parameter and the lattice parameter. On the other hand, the bond lengths are related with the inversion parameter. Using changes of the lattice parameter during irradiation we have calculated the inversion parameter, which is 15–20%. In the luminescence spectra, the fast neutron radiation (fluence 10^{16} cm^{-2}) produces an increase in the intensity ratio of the N- to R-lines by 5–20%. Taking into account that intensity of the N-lines is closely associated with the inversion parameter, it is possible to state that the neutron irradiation causes the increasing of the spinel inversion. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Magnesium aluminium spinel; Neutron irradiation; Luminescence spectra; Inversion parameter

1. Introduction

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 [1–3]. $MgAl_2O_4$ thin film is a possible candidate for the development of integrated humidity sensors [4]. Spinel single crystals are used for substrate in integrated electronics [5], they are known as laser materials [6–9].

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 centered 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^7_h and is called "normal". The octahedral and tetrahedral sites of the spinel structure are shown in Fig. 1. 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. The cation disorder phenomenon has been investigated by various methods [10–13]. If we use an inversion parameter i, the chemical

* Corresponding author. Tel.: +371-7980022; fax: +371-7901212.

E-mail addresses: vskv@delfi.lv, vskv@mail.ru (V. Skvortsova).

PII: S0168-583X(02)00571-2

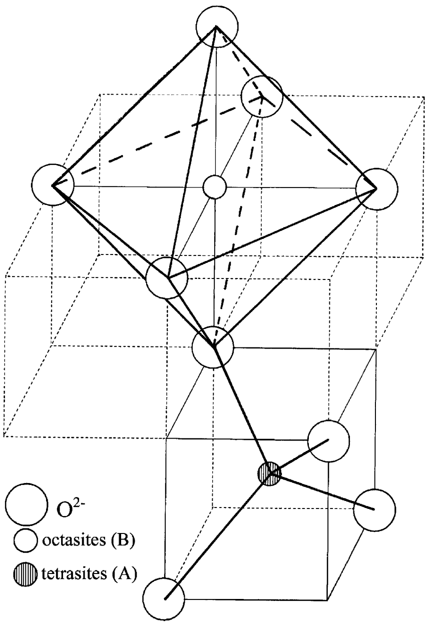

Fig. 1. Octahedral and tetrahedral sites in spinel structure.

formula of magnesium aluminium spinel may be expressed by $(Mg_{1-i}Al_i)[Mg_iAl_{2-i}]O_4$, assuming $i = 1$, we obtain a formula $Al[MgAl]O_4$ for the inverse spinel.

This paper present results of investigation of the inversion parameter using the changes of the lattice parameter and luminescence spectra of magnesium aluminium spinel caused by the irradiation with fast neutrons.

2. Experimental

$MgO \cdot nAl_2O_3$ single crystals were grown by the Verneuil method. The sample thickness was in the range of 0.5–1 mm. Crystals labeled as 'Mn' have been doped with manganese. Natural spinel crystals from the Ural mountains were used. Micro (Cr, Mn, Fe) and macrocomponent (Mg, Al) quantities have been detected by the instrumental neutron activation analysis technique [14]. Concentrations of some impurities (mass %) are given in Table 1. Table 2 presents the results of the determination of the macrocomponents and lattice parameters in the magnesium–aluminium spinels. The X-ray diffraction spectra were measured by diffractometer DRON-UM2 (USSR) using CuKα-radiation ($U = 40$ kV, $I = 20$ mA). A computer connected with the diffractometer was used for logging and processing of data.

Table 1
Concentration of impurities (in mass %)

Type	Cr	Mn	Fe
Natural	2×10^{-3}	2.9	0.31
$MgO \cdot Al_2O_3$ (1)	0.43×10^{-4}	0.3×10^{-4}	1×10^{-3}
$MgO \cdot Al_2O_3$ (2)	0.41×10^{-4}	0.16×10^{-4}	8.1×10^{-4}
$MgO \cdot 2Al_2O_3$	1.25×10^{-4}	0.17×10^{-4}	4×10^{-4}
$MgO \cdot 2.8Al_2O_3$	0.99×10^{-4}	0.2×10^{-4}	–
$MgO \cdot 2.5Al_2O_3Mn0.1$	1×10^{-4}	3.0×10^{-2}	1.4×10^{-2}

Table 2
Contents of macrocomponents in spinel and lattice parameters

Type	Introduced	Obtained	a (nm)
$MgO \cdot Al_2O_3$ (2)	1:1	1:0.9	0.8061
$MgO \cdot 2Al_2O_3$	1:2	1:1.7	0.8006
$MgO \cdot 2.8Al_2O_3$	1:2.8	1:2.5	0.7995

The luminescence spectra of spinel crystals have been measured at liquid nitrogen temperature with an SPM-2 monochromator having a diffraction grating of 651 line per mm. The crystals were excited by the high pressure xenon lamp (DKSEL-1000) connected to the 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} cm^{-2}. The accompanied γ-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.

3. Results and discussion

The results of the lattice parameter measurements are given in Table 3.

The fast neutron irradiation of magnesium aluminium spinel leads to the decrease of the lattice parameter. This phenomenon was described in paper [5,15,16]. In the spinel structure, the oxygen

Table 3
Lattice parameter before and after fast neutron irradiation (fluence $\phi = 10^{20}$ cm^{-2})

Notation	a (nm) (before irradiation)	a (nm) (after irradiation)
$MgO \cdot Al_2O_3$ (1)	0.80887	0.80113
$MgO \cdot 2.5Al_2O_3Mn0.1$	0.80770	0.80122

ion is surrounded by four cations, with one occupying the A site and other the three occupying B sites [17]. The bond lengths of A–O and B–O vary with the u parameter and lattice parameters.

$$\mathrm{A{-}O} = \sqrt{3}a\left(u - \frac{1}{4}\right), \tag{1}$$

$$\mathrm{B{-}O} = a\sqrt{\left(u - \frac{5}{8}\right)^2 + 2\left(u - \frac{3}{8}\right)^2}. \tag{2}$$

On the other hand, the bond lengths are connected with the inversion parameter [18]. The bond lengths $(\mathrm{A{-}O})_T$ and $(\mathrm{B{-}O})_T$ at the temperature T may be expressed by

$$(\mathrm{A{-}O})_T = id(^{\mathrm{IV}}\mathrm{Al})[1 + \alpha_{\mathrm{Al}}(T - 20)] + (1 - i)d(^{\mathrm{IV}}\mathrm{Mg})[1 + \alpha_{\mathrm{Mg}}(T - 20)], \tag{3}$$

$$(\mathrm{B{-}O})_T = \frac{i}{2}d(^{\mathrm{VI}}\mathrm{Mg})[1 + \beta_{\mathrm{Mg}}(T - 20)] + \left(1 - \frac{i}{2}\right)d(^{\mathrm{VI}}\mathrm{Al})[1 + \beta_{\mathrm{Al}}(T - 20)], \tag{4}$$

where $d(^{\mathrm{IV}}\mathrm{Mg})$ and $d(^{\mathrm{IV}}\mathrm{Al})$ are the bond lengths of the four-coordinated Mg and Al at 20 °C, respectively; likewise, $d(^{\mathrm{VI}}\mathrm{Mg})$ and $d(^{\mathrm{VI}}\mathrm{Al})$ are the bond lengths of these atoms for the six-coordinated cases. The α_{Al}, α_{Mg}, β_{Mg}, β_{Al} are thermal expansion coefficients of the bonds $^{\mathrm{IV}}$Mg–O, $^{\mathrm{IV}}$Al–O, $^{\mathrm{VI}}$Mg–O, $^{\mathrm{VI}}$Al–O. Eqs. (3) and (4) becomes simpler, if $T = 20$ °C. Solving Eqs. (1), (3) and (2), (4) together we obtain the expression for the determination of the inversion parameter. For bond lengths at 20 °C we may put the following values: $d(^{\mathrm{VI}}\mathrm{Mg}) = 0.2115$ nm [19], $d(^{\mathrm{VI}}\mathrm{Al}) = 0.1909$ nm [19], parameter $u = 0.3873$ [18]. Using the changes of the lattice parameters during irradiation we have calculated the inversion parameter. For $MgO \cdot Al_2O_3$ single crystal it is ~18%, for $MgO \cdot 2.5Al_2O_3Mn0.1$ ~15%.

Radiation produces both ionisation and displacement damage in $MgAl_2O_4$ [20]. In the case of $MgAl_2O_4$ only octahedral cation vacancies have been proposed [21], however, due to the cation disorder the coexistence of both octahedral and tetrahedral cation vacancies is possible [22]. The fast neutron irradiation leads to replacement of aluminium ions by magnesium ones and causes formation of cation vacancies necessary for maintenance of charge neutrality. The appearance of octahedrally and tetrahedrally coordinated cation vacancies in spinel structure affects the local symmetry of impurity ions such as Cr^{3+} which are present in all our crystals (see Table 1). Cr^{3+} has a large preference energy to a octahedral site and almost always substitutes only for the octahedral sites in all spinel structures.

The photoluminescence spectra of natural and two synthetic spinels $MgO \cdot Al_2O_3$ and $MgO \cdot 2.8Al_2O_3$ are given in Fig. 2. In the natural spinel spectra some zero-phonon lines were observed in the region of the Cr^{3+} ions electron transition $^2E_g \to {}^4A_{2g}$: 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 [23]; N-lines (686.0, 688.2, 690.9 and 692.3 nm) related to the Cr^{3+} ions the local symmetry of which differs from symmetry of sites occupied by Al^{3+} in normal spinel (Fig. 2, curve 1). The broadening of R- and N-lines takes place in synthetic stoichiometric spinel. Supposing that some of the nearest cations of a Cr^{3+} ion are substituted by Mg^{2+} ions, the distorted crystal field influences the chromium ion. Then Cr^{3+} emission is shifted to longer wavelength side. The displaced lines are called N-lines [24]. If considerable number of Mg and Al cations has substituted one for another in a crystal, there will be less normally arranged Cr^{3+} ions in this crystal. Then the R- and N-lines draw nearer. The lines of the phonon-assisted sideband become broadened, too. The effect appears in a luminescence emission spectrum of a synthetic stoichiometric spinel (Fig. 2, curve 2). The changes in intensities and broadening of the luminescence lines are more pronounced in non-stoichiometric spinels. Structure

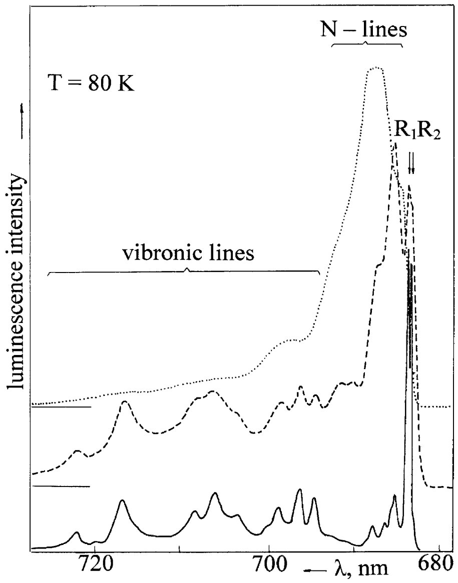

Fig. 2. Photoluminescence spectra of magnesium aluminium spinel. Solid line: natural spinel; dashed line: synthetic crystal $MgO \cdot Al_2O_3$; dotted line: synthetic crystal $MgO \cdot 2.8Al_2O_3$.

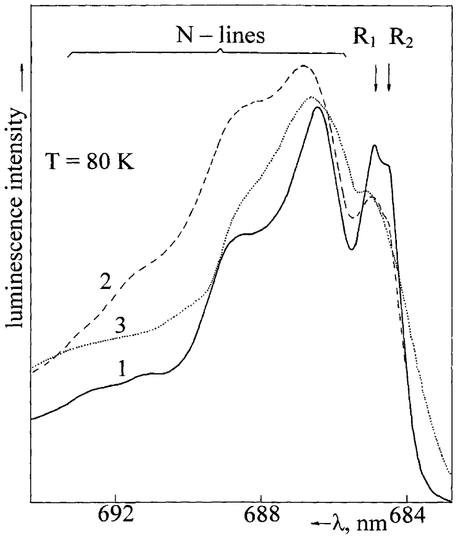

Fig. 3. Photoluminescence spectra of magnesium aluminium spinel $MgO{\cdot}Al_2O_3$ in the zero–phonon line region. Solid line: before irradiation; dashed line: after irradiation by fast neutron fluence 10^{16} cm^{-2}; dotted line: after irradiation by fast neutron fluence 10^{20} cm^{-2}.

of synthetic non-stoichiometric 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 number 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 non-stoichiometric spinel one can observe the highly broadened bands with rather intensive N-lines and without signs of R-lines (Fig. 2, curve 3).

The broadening of R- and N-lines takes place after spinel crystals irradiation by fast neutron. The photoluminescence spectra of magnesium aluminium spinel $MgO \cdot Al_2O_3$ are shown in Fig. 3. In the luminescence spectra of $MgO \cdot Al_2O_3$, the fast neutron irradiation (fluence 10^{16} cm^{-2}) produces an increase in the intensity ratio of N- to R-lines by 5–20%. At fluence 10^{20} cm^{-2} the spectra structure cannot be clearly seen, so the zero-phonon lines are not resolved and the integral intensity of Cr^{3+} luminescence decreases. We observed the same changes of the Cr^{3+} luminescence in non-stoichiometric spinel. 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.

4. Conclusion

The photoluminescence spectra of stoichiometric and non-stoichiometric magnesium aluminium spinel containing small concentration of chromium ions are investigated. It should be noted that the fast neutron irradiation causes the increasing of the spinel inversion. It is estimated as 5–20% at fast neutron fluence of 10^{16} cm^{-2}. During irradiation the lattice parameters have changed, which variations are used for calculating the inversion parameter to be 15–20%.

Acknowledgements

The research was financially supported by the Latvian Council of Science (grant no. 96.0412 and project no. 01-0806).

References

[1] R.H. Gouiding, S.J. Zincle, D.A. Rasmussen, R.E. Stoller, J. Appl. Phys. 79 (1996) 2920.
[2] F. Ayeres de Oliveira Neto, S. Soares de Souza, A.R. Blak, Radiation Protection Dosimetry 84 (1999) 139.
[3] W.A. Coghlan, F.W. Clinard Jr., N. Itoh, et al., J. Nucl. Mater. 141–143 (1986) 382.
[4] G. Gusmano, G. Montesperelli, E. Traversa, G. Mattogno, J. Am. Ceram. Soc. 76 (1993) 743.
[5] C.C. Wang, J. Appl. Phys. 40 (1969) 3433.
[6] K. Petermann, R. Clausen, E. Heumann, et al., Opt. Commun. 70 (1989) 483.
[7] R. Clausen, K. Petermann, IEEE J. Quantum Electronic 24 (1988) 1114.
[8] C. Wyon, J.J. Aubert, F. Auzel, J. Cryst. Growth 79 (1986) 710.
[9] B.K. Sevastyanov, The 8th Feofilov Symposium on Spectroscopy of Crystals Doped with Rare-Earth and Transition Metal Ions, 1985, p. 117.
[10] S. Hafner, Z. Krustallogr. 115 (1960) 331.
[11] U. Schmocker, H.R. Boesch, F. Waldner, Phys. Lett. 40a (1972) 237.
[12] A.N. Cormack, G.V. Lewis, S.C. Parker, C.R.A. Catlow, J. Phys. Chem. Solids 49 (1988) 53.
[13] R.W. Grimes, A.B. Anderson, A.H. Heuer, J. Amer. Chem. Soc. 111 (1989) 2168.
[14] V. Skvortsova, D. Riekstina, Adv. Sci. Technol., Faenza 19 (1999) 245.
[15] V.N. Vetrov, B.A. Ignatenkov, E.N. Ryzhikov, Izv. Akad. Nauk. SSSR, Neorg. Mater. 24 (1988) 516.
[16] R.L. Molner, W.B. White, J. Electrochem. Soc. 142 (1995) 3923.
[17] S. Krupichka, Physics of ferrite and related magnetic oxides. Moscou,1975.
[18] T. Yamanaca, Y. Takeuchi, Z. Kristallogr. 165 (1983) 65.
[19] V.M. Talanov, Kristallografija 24 (1979) 706 (in Russian).
[20] G.P. Pells, J. Nucl. Mater. 184 (1991) 177.
[21] R. Dupree, M.H. Levis, M.E. Smith, Philos. Mag. A 53 (1986) L17.
[22] A. Ibarra, R. Vila, M. Jimenez de Castro, Philos. Mag. Lett. 64 (1991) 45.
[23] D.L. Wood, G.F. Imbush, R.M. Macfarlane, et al., J. Chem. Phys. 48 (1968) 307.
[24] W. Mikenda, A. Preisinger, J. Luminescence 26 (1981) 53.