

Transformation of spinel crystals structure $\text{MgO} \cdot n\text{Al}_2\text{O}_3$ under high-temperature annealing

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The processes at high temperature annealing of non-stoichiometric $\text{MgO} \cdot n\text{Al}_2\text{O}_3$ spinel crystals ($n = 2.2$) in O_2 atmosphere at 1300–1500°C have been investigated. A gradual non-stoichiometry increase up to $n = 2.8$ has been found with increasing annealing time due to MgO evaporation followed by formation of polycrystalline $\alpha\text{-Al}_2\text{O}_3$ phase. The structure and composition $\text{MgO} \cdot n\text{Al}_2\text{O}_3$ layer grown at the sapphire surface in MgO vapor of at 1500–1800°C have been studied. The formation of amorphous phase in transition zone from hexagonal sapphire structure with a piling sequence ABABAB into spinel cubic one with sequence of atomic layers ABCABC was established.

Исследованы процессы высокотемпературного отжига кристаллов нестехиометрической шпинели $\text{MgO} \cdot n\text{Al}_2\text{O}_3$ ($n = 2,2$) в атмосфере O_2 при 1300–1500°C. Установлено постепенное увеличение нестехиометрии кристаллов до $n = 2,8$ с увеличением времени отжига вследствие испарения MgO и последующего образования поликристаллической фазы $\alpha\text{-Al}_2\text{O}_3$. Исследованы структура и состав слоев $\text{MgO} \cdot n\text{Al}_2\text{O}_3$, выращенных на поверхности сапфира в парах MgO при 1500–1800°C. Установлено формирование аморфной фазы в зоне перехода из гексагональной структуры сапфира с последовательностью укладки слоев ABABAB в кубическую структуру шпинели с последовательностью укладки атомных слоев ABCABC.

Magnesium aluminate spinel is used widely due to combination of dielectric and optical properties, hardness, durability, density, resistance against high temperature corrosion and radiation. Spinel is recommended for application as a component in forms for storage of nuclear wastes [1], and nuclear fuel [2], as an inert matrix for transmutation of actinides [3], as insulator for magnetic coils [4] and windows for radio frequency heating plasma in reactors [5]. In any indicated applications, this material is subjected to high-temperature aggressive media which may cause changes in functional properties of devices. The purpose of this work is to study the crystal structure changes of magnesium aluminate spinel

under high-temperature annealing in oxygen atmosphere using X-ray diffraction (XRD), namely, the composition changes and phase transformations. These transformations were investigated across the thickness of spinel layer obtained on the sapphire surface ($\alpha\text{-Al}_2\text{O}_3$) at high-temperature annealing in MgO vapor.

It is known that magnesium aluminates spinel crystals MgAl_2O_4 or $\text{MgO} \cdot n\text{Al}_2\text{O}_3$ are of cubic structure and could be formed in the wide ratio range of constituent oxides ($n = 1.0\text{--}7.3$) [6]. In stoichiometric crystals ($n = 1.0$), Mg^{2+} ions occupy mainly tetrahedral positions formed by oxygen ions, Al^{3+} ions are situated mainly in octahedral sites. As the crystal composition deviates from

stoichiometric one ($n > 1.0$), the spinel structure is formed with excess of cationic vacancies, mainly in octahedral positions [7]. If in MgAl_2O_4 spinel all Mg^{2+} ions are replaced by Al^{3+} ones, then, according to charge compensation, the reaction $\text{Mg}^{2+}_{tetra} = I_{1/3} + \text{Al}^{3+}_{2/3}$ takes place, where I is unoccupied cation vacancy. As a result, a defect spinel structure corresponding to oxide $\gamma\text{-Al}_2\text{O}_3$ is formed [8], which usually is considered as the limit composition of this solid solution line. As the Al_2O_3 content increases, the lattice parameter in non-stoichiometric spinel crystal is diminished. To date, several equations have been proposed for dependence of the lattice parameter (a) on the degree of deviation extent of spinel composition from stoichiometric one (n). The dependences $a = f(n)$ was derived mainly from the limit composition of the continuous sequence of solid solutions including the stoichiometric magnesium aluminate spinel $\text{MgO}\cdot\text{Al}_2\text{O}_3$ and aluminum oxide $\gamma\text{-Al}_2\text{O}_3$. The knowledge of precise dependence $a = f(n)$ could be used to determine the spinel composition basing on precisely measured lattice parameter.

In [6], the following equation has been proposed for $a = f(n)$ which describes well the experimental data of the authors:

$$a = a_0 - 18.660(n - 1)/M, \quad (1)$$

where a_0 is the lattice parameter of stoichiometric spinel ($a_0 = 8.086 \text{ \AA}$); M , the molecular mass of non-stoichiometric spinel. In [9], another expression was proposed:

$$a = \frac{a_0 + 3(n - 1)a_1/4}{1 + 3(n - 1)/4}, \quad (2)$$

where a_1 is the lattice parameter of aluminum oxide $\gamma\text{-Al}_2\text{O}_3$ ($a_1 = 7.922 \text{ \AA}$). Finally, according to [10] the n value as a function of lattice parameter is described as

$$n = \frac{8.61109 - a}{3a - 23.7195}. \quad (3)$$

We have used all three expressions to calculate the function $a = f(n)$. In Fig. 1, we present this function is presented as averaged calculated values using the empirical expressions (1–3). We have used also data from other sources on the measured lattice parameter values for spinels of different compositions [11–13] and plotted the averaged experimental data. We found that none of empirical formulae (and thus none

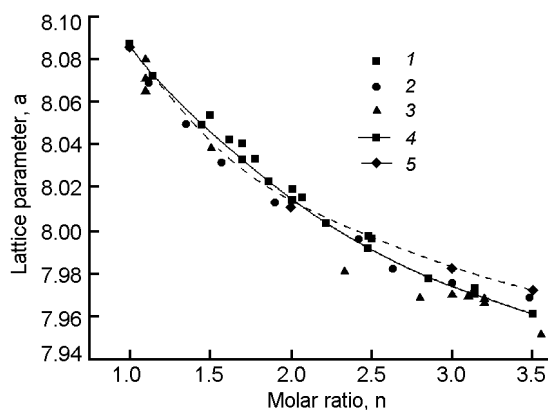


Fig. 1. Dependences of lattice parameter on composition ($a = f(n)$) for magnesium aluminate spinel crystals. 1 – [12], 2 – [11], 3 – [13], 4 – averaged experimental data, 5 – averaged calculated data.

of averaged empirical curves) does not coincide with experimental one. Therefore, in this work, the experimental curve was used to determine the influence of changes in the spinel crystal composition on the measured lattice parameter.

Non-stoichiometric spinel crystals $\text{MgO}\cdot 2.2\text{Al}_2\text{O}_3$ grown by Verneuil methods were polished to optical quality and annealed in oxygen atmosphere at 1500°C or 1300°C for different time. The spinel layers were obtained at the sapphire surface during the annealing in MgO vapor at $1550\text{--}1800^\circ\text{C}$.

The spinel layers modified by annealing or obtained on the sapphire surface were examined using a DRON-3M diffractometer. To determine the lattice parameter, the diffraction angle was measured at the diffractational reflection center of X-ray line $\text{Cu}_{K\alpha 1} = 1.54051 \text{ \AA}$ from the (931) plan using 0.05 mm slit width. The lattice parameter measurement accuracy was $2 \cdot 10^{-4} \text{ \AA}$. X-ray phase analysis of spinel layers was provided from XRD pattern taken in $\theta - 2\theta$ mode in the 2θ angle range $0\text{--}80^\circ$ using 0.25 mm slit width.

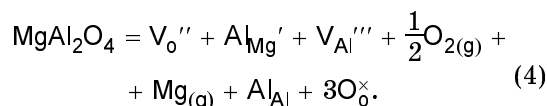
In non-stoichiometric spinel crystals $\text{MgO}\cdot 2.2\text{Al}_2\text{O}_3$ annealed in oxygen atmosphere at 1500°C , the lattice parameter was measured and composition of crystals was derived using Fig. 1 (Table). It can be seen that increasing the annealing time of during 0.5 and 1.0 hour results in increasing deviation of crystal composition from stoichiometric one. The annealing at lower temperature 1300°C but for a longed time (3 h) results in formation of more non-stoichiometric ($n = 2.8$) and thin layer of

Table. The changes in lattice parameter (a) and composition (n) of spinel crystals $\text{MgO} \cdot n\text{Al}_2\text{O}_3$ after annealing in oxygen atmosphere

T , °C	t , hour	2θ , deg	a , Å	n
As-grown	–	133.36	8.0014	2.2
1500	0.5	133.5	7.9972	2.3
1500	1	133.72	7.9906	2.5
1500	10	Polycrystalline $\alpha\text{-Al}_2\text{O}_3$		
1300	3	134.01	7.982	2.8
Spinel + polycrystalline $\alpha\text{-Al}_2\text{O}_3$				

polycrystalline phase of $\alpha\text{-Al}_2\text{O}_3$ at the spinel crystal surface. At the XRD pattern, the maxima of reflections from (104) and (110) plans in polycrystalline $\alpha\text{-Al}_2\text{O}_3$ are seen and at the same time the reflection from (311) in spinel single crystal is present (Fig. 2). The measured lattice parameter $a = 7.982 \text{ \AA}$ which corresponds to $n = 2.8$. We can suppose that at $n = 2.8$, a formation possibility of polycrystalline $\alpha\text{-Al}_2\text{O}_3$ at the spinel crystal surface occurs. Finally, annealing during 10 hours at 1500°C causes formation of polycrystalline $\alpha\text{-Al}_2\text{O}_3$.

The diffusion activity of Mg^{2+} cations and evaporation of MgO from the crystal surface are in accordance to the reaction:



It is quite possible that the evaporation process could cause the critical concentration of aluminum oxide and formation of $\gamma\text{-Al}_2\text{O}_3$ having cubic lattice structure, which transforms into hexagonal $\alpha\text{-Al}_2\text{O}_3$ structure near 1000°C .

The calculated lattice parameter for $n = 7$ spinel solid solution is $a = 7.93 \text{ \AA}$, the lattice parameter of AlAl_2O_4 aluminum spinel according to [14] is $7.915\text{--}7.92 \text{ \AA}$. Finally, the calculated lattice parameter of $\gamma\text{-Al}_2\text{O}_3$ [15] is 7.911 \AA . When all cations are situated in the octa-position, this structure has minimum energy. In real $\gamma\text{-Al}_2\text{O}_3$ crystals, cations occupy both the tetra- and octa-positions in 63:37 ratio, but in $\alpha\text{-Al}_2\text{O}_3$ structure, all cations are situated in octa-positions. The question remains open what the spinel structure phase precedes the $\alpha\text{-Al}_2\text{O}_3$ formation. Therefore, at the annealing of non-stoichiometric spinel crystals $\text{MgO} \cdot 2.2\text{Al}_2\text{O}_3$ in oxidizing atmosphere the

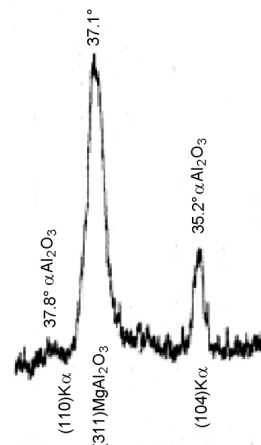


Fig. 2. XRD pattern of $\text{MgO} \cdot 2.2\text{Al}_2\text{O}_3$ spinel crystals annealed in oxygen indicating the presence of $\alpha\text{-Al}_2\text{O}_3$ phase and $\text{MgO} \cdot 2.8\text{Al}_2\text{O}_3$ spinel.

polycrystalline $\alpha\text{-Al}_2\text{O}_3$ was formed along with $n = 2.8$ spinel.

The transformation of sapphire structure into the magnesium aluminate spinel one was observed at the annealing in MgO vapor in the temperature range of $1550\text{--}1800^\circ\text{C}$. At the surface of annealed single crystals, a thin layer of polycrystalline magnesium aluminate spinel was formed as a result of solid-phase reaction. The layer thickness was changed from 20 to $300 \mu\text{m}$ depending on the annealing duration [16]. Similar experiments were carried out before, where sapphire was annealed in hydrogen atmosphere and MgO vapor in the $1500\text{--}1900^\circ\text{C}$ temperature range [17]. Our XRD investigations have shown the practically constant lattice parameter $a = 8.082 \text{ \AA}$ over the whole sample surface, which corresponds to lattice parameter of stoichiometric spinel ($n = 1.0$) (Fig. 3a). After taking off the near-surface layer at approximately $20 \mu\text{m}$ and duplicate measurement, the XRD pattern shows much smaller lattice parameter

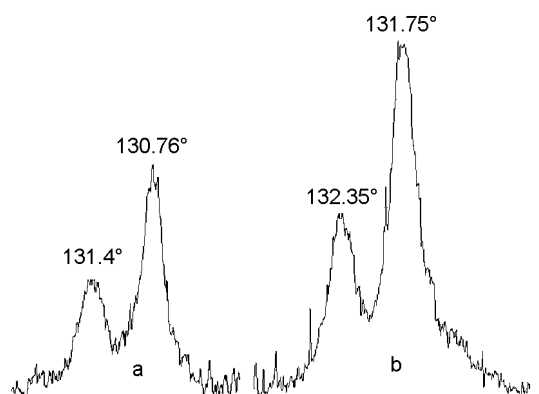


Fig. 3. XRD pattern in the region of (931) diffraction maximum from initially obtained spinel layer (a) and after taking off 20 μm near-surface layer (b).

value $a = 8.051 \text{ \AA}$ corresponding to spinel with $n = 1.5$ (Fig. 3b).

The stroke XRD patterns for two neighboring spots (at 2 mm distance) on the annealed sample surface indicates the existence of differently oriented spinel crystal grains on the sapphire surfaces. In one case, the primarily [111] orientation of spinel crystal grain growth was registered (Fig. 4.1), in another case, the [110] orientation was found (Fig. 4.2). The taking off of surface layers by lapping of crystals followed by XRD measurements disclose that at the initial stage of spinel layer growth, the (111) plans of spinel (Fig. 4.3) are oriented predominantly in parallel to (0001) plans of sapphire [18]. With increasing spinel layer thickness, the formation of growth texture or predominant crystal orientation takes place. Those crystal grains showing trend to maximal growth rate along the normal to crystallization front replace all others [19].

According to [17], magnesium aluminate spinel layer formed at the sapphire annealing in hydrogen atmosphere and MgO vapor has variable composition through its thickness. The transition layer was changing from the stoichiometric composition at the outer surface ($n = 1.0$) to the inner boundary reaching $n = 3.0$ in the transition zone from hexagonal sapphire structure to spinel cubic one. A peculiarity of the transition zone is a sharp decrease of microhardness which may indicate the amorphous structure of this zone.

Our data also indicate the decrease of spinel lattice parameter in sub-layer situated near the transition zone. The diffraction maxima from (111) plans of spinel as

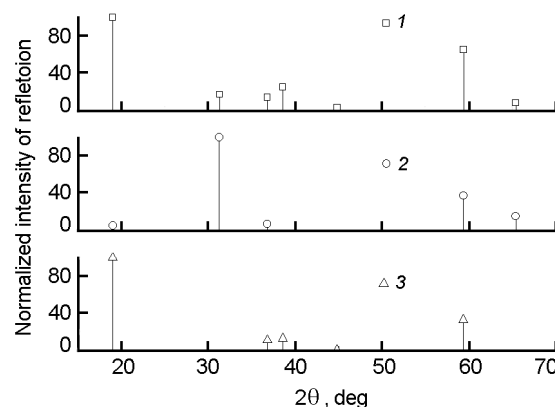


Fig. 4. Stroke XRD patterns for two neighboring spots on the crystal surface: 1, [111] orientation; 2, [110] orientation; 3, transition zone.

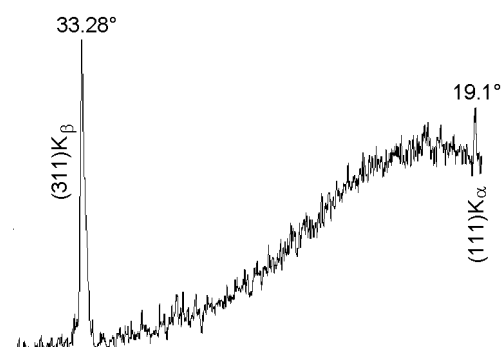


Fig. 5. XRD pattern from transition layer between hexagonal sapphire lattice and cubic spinel lattice.

the first, second, and third order reflections are clearly seen in the XRD pattern from transition zone. This indicates the diffraction from anionic sub-lattice. The diffraction maxima from other plans of magnesium aluminate spinel have lower intensity and are fuzzy. A broad diffraction maximum at small angles was observed too, which corresponds to 2–4 \AA interatomic distance range (Fig. 5).

Usually, a circle at Bragg angle was observed in XRD patterns from amorphous sample and the interatomic distances (d) are ranged 2–5 \AA according to Wulf-Bragg relation [20]. Our data allow to estimate d in amorphous spinel layer. The diffusion background shows a maximum at $2\theta = 21^\circ$ that corresponds to $d = 4.225 \text{ \AA}$. At the same time, a diffraction maximum at $2\theta = 19.1^\circ$ from anionic sub-lattice also can be seen corresponding to $d = 4.64 \text{ \AA}$ distance between oxygen ions O^{2-} in the spinel struc-

ture lattice. The difference $\Delta d = 0.415 \text{ \AA}$ could be related to distortion of spinel lattice at the 9 % level. Indeed, the distance between anions in hexagonal close-packed lattice is 8 % smaller as compared to cubic spinel [21] and this difference results in formation of an amorphous layer of some thickness and as consequence in polycrystalline spinel growth at non-stoichiometric composition.

Thus, the transition from sapphire of hexagonal close-packed ABABAB sequence into cubic spinel with sequence of atomic layers ABCABC does not occur by twinning [18] or by shift of oxygen atoms which take place in martensitic transformation [19] but due to disordering structure like amorphous state.

The characteristic structure changes in magnesium aluminate spinel were observed in [22]. Under irradiation with 340 keV Xe^{++} ions at 100 K at fluence over $5 \cdot 10^{18}$ ions/m², which corresponds to 1.2 displacements per atom (dpa), a metastable phase was observed to be formed. This phase is similar in structure to rock-salt of $Fm\bar{3}m$ space group where cations occupy randomly octahedral position, but tetrahedral position are free. Just after the critical concentration of vacancies in anionic sublattice is accumulated, the phase transition into metastable phase becomes energy favorable. After irradiation at fluence up to $1 \cdot 10^{20}$ ions/m², the spinel sample becomes amorphous and the spinel hardness drops down by 60 %.

The experiments demonstrate the reversible transformation of spinel structure into corundum one under annealing of $\text{MgO} \cdot n\text{Al}_2\text{O}_3$ single crystals in oxidizing atmosphere and inverse process, the growth of polycrystalline spinel layer on sapphire at the annealing in MgO vapor. Mg^{2+} cations get out from spinel lattice with displacement of those ions from tetra-sites into octa-sites, transport to surface and finally leave the crystal. At the sapphire annealing in MgO vapor in the transition zone of hexagonal sapphire lattice into cubic spinel lattice, an amorphous layer forms containing Mg, Al, and O atoms. The amorphization takes place due to strong distortion of anionic sublattice in the rearrangement by sequential lapping of ABABAB arrangement on

ABCABC one. The composition of spinel layers obtained on the sapphire changes from stoichiometric $n = 1.0$ at the surface to non-stoichiometric $n = 1.5$ in transition zone. In the transition zone, the orientation of plans is homogeneous over the sample surface, but with increasing layer thickness, the growth texture appears.

References

1. E.A.C.Neeft, R.J.M.Konings, K.Bakker et al., *J. Nucl. Mater.*, **274**, 78 (1999)
2. Y.Lee, S.C.Lee, H.S.Kim, C.Y.Joung, *J. Nucl. Mater.*, **319**, 15 (2003).
3. F.C.Klaassen, K.Bakker, R.P.C.Schram et al., *J. Nucl. Mater.*, **319**, 108 (2003).
4. G.P.Pells, *MRS Bulletin*, 22 (1997).
5. F.A.Garner, G.W.Hollenberg, F.D.Hobbs et al., *J. Nucl. Mater.*, **212–215**, 1087 (1994).
6. V.N.Vetrov, B.A.Ignatenko, E.N.Ryzhikov et al., *J. Neorg. Mater.*, **24**, 516 (1988).
7. R.Basso, S.Carbonin, A.Della Guista, *Zeitschr. Kristallogr.*, **194**, 111 (1991).
8. S.Krupichka, *Physics of Ferrites*, Moscow (1976) [in Russian].
9. Jing Shou-Yong, Lin Li-Bin, Huang Ning Kang et al., *J. Mater. Sci. Lett.*, **19**, 225 (2000).
10. Ching-Jui Ting, Hong-Yang Lu, *J. Amer. Ceram. Soc.*, **83**, 1592 (2000).
11. A.Navrotsky, B.A.Wechsler, K.Geisinger, F.Seifert, *J. Amer. Ceram. Soc.*, **69**, 158 (1986).
12. C.C.Wang, *J. Appl. Phys.*, **40**, 3433 (1969).
13. R.I.Sheldon, T.Hartmann, K.E.Sickafus et al., *J. Amer. Ceram. Soc.*, **82**, 3293 (1999).
14. N.S.Sidelnikova, M.A.Rom, A.Ya.Dan'ko et al., *Functional Materials*, **11**, 26 (2004).
15. G.Gutierrez, A.Tagar, B.Johanson, *Phys. Rev.*, **B65**, 012101 (2001).
16. E.P.Andreev, V.B.Kolner, P.V.Konevskij et al., in: Abstracts of Inter. Conf. "Crystal Materials'2007", Kharkov, Ukraine, 2007, p.121.
17. L.Navias, *J. Amer. Ceram. Soc.*, **44**, 434 (1961).
18. C.B.Carter, H.Schmalzried, *Phil. Mag.*, **A52**, 207 (1985).
19. L.S.Palatnik, I.I.Papirov, *Orientation Crystallization*, Nauka, Moscow (1964) [in Russian].
20. A.Ginje, *Roentgenography of Crystals*, Nauka, Moscow (1961) [in Russian].
21. E.Dobrovinskaja, L.Litvinov, V.Pischik, *Encyclopedia of Sapphire*, Kharkov (2004) [in Russian].
22. I.V.Afanasyev-Charkin, R.M.Dickerson, D.W.Co-oke et al., *J. Nucl. Mater.*, **289**, 110 (2001).

Перетворення структури кристалів шпінелі $\text{MgO} \cdot n\text{Al}_2\text{O}_3$ при високотемпературному відпалі

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Досліджено процеси високотемпературного відпалу нестехіометричних кристалів шпінелі $\text{MgO} \cdot 2\text{Al}_2\text{O}_3$ в атмосфері O_2 при 1300–1500°C. Виявлено поступове збільшення нестехіометрії кристалів до $n = 2,8$ зі збільшенням часу відпалу внаслідок випаровування MgO з наступним формуванням полікристалічної фази $\alpha\text{-Al}_2\text{O}_3$. Досліджено структуру та склад шарів $\text{MgO} \cdot n\text{Al}_2\text{O}_3$, вирощених на поверхні сафіру в парах MgO при 1500–1800°C. Встановлено формування аморфної фази у зоні переходу від гексагональної структури сафіру з послідовністю укладки шарів АВАВАВ у кубічну структуру шпінелі з послідовністю укладки атомних шарів АВСАВС.