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Structural and mechanical characteristics of magnesium-aluminate spinel crystals grown by Verneuil and Czochralski methods

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The investigations of X-ray diffraction in magnesium aluminate spinel crystals of stoichiometric and non-stoichiometric compositions grown by Verneuil method were provided. It was revealed the decrease of MgO content at periphery to compare with that of center of crystals. The block structure of these crystals was revealed and the origin of it is discussed. There were also investigated spinel crystals grown by Czochralski method as nominally pure and doped with Mn to concentrations of 0.02, 0.04, and 0.1 mass.%. The absence of variation of composition across of radius of crystals in Czochralski grown spinel crystals was observed. More high mechanical parameters were obtained for Czochralski grown crystals.

Проведены рентгеновские дифрактометрические исследования кристаллов магний-алюминиевой шпинели стехиометрического и нестехиометрического состава, выращенных методом Вернейля. Радиальное распределение состава кристаллов показывает уменьшение содержания MgO на периферии кристалла по сравнению с его центром. Обнаружена блочная структура этих кристаллов и обсуждается ее природа. Исследованы кристаллы магний-алюминиевой шпинели, выращенные методом Чохральского, номинально чистые и легированные Mn до концентраций 0,02; 0,04 и 0,1 масс.%. Обнаружено отсутствие изменения состава вдоль радиуса кристаллов, выращенных методом Чохральского. Более высокие механические характеристики получены для кристаллов, выращенных методом Чохральского.

Due to excellent physical and chemical properties of spinel crystals they are very attractive for application in science and technology. Particularly, spinel crystals are considered as substrates for microelectronics [1], matrices for fabrication of optical nano-devices [2] and high brightness and good contrast phosphor screens [3], fiber-optics temperature sensors [4], etc. The crystalline structure of $MgAl_2O_4$ spinel is a face-centered cubic lattice of oxygen ions. The unit of spinel consists of 8 molecules $MgAl_2O_4$ and 32 oxygen ions form 64 tetrahedral and 32 octahedral sites, which are occupied by eight Mg^{2+} ions and sixteen Al^{3+} ions, respectively. Such cationic distribution is called "normal" and observed only in natural spinel crystal, but in synthetic crystals up to 30 % of pairs of magnesium and aluminum ions interchange their position leading to formation of partially "inverse" spinel structure. Besides this, spinel structure could be formed in the wide range mole concentration of constituent oxides $MgO{\cdot}nAl_2O_3$ of $1.0 \le n \le 3.5$ which leads to formation of additional cationic vacancies in spinel lattice. Both facts are dependent on the crystal growth conditions and define

the final properties of grown crystals. In this work we provided the comparative investigations of structural and mechanical characteristics of spinel crystals grown from the same starting materials by Verneuil and Czochralski methods.

The precision measurements of lattice parameters were conducted by using diffractometer DRON-3M in radiation of the copper anode. There was used a reflection from planes (931) at the angle of diffraction $2\theta = 130.78°$. The good resolution of $K_{\alpha 1}$ and $K_{\alpha 2}$ doublet has allowed to calculate the center of gravity of diffraction line from $CuK_{\alpha 1}$ radiation with the wavelength $\lambda = 1.54051$ Å. Because the crystals grown by Verneuil method are block-like, there were used narrow slits equal to 0.05 mm on collimator and counter which allowed tracking the variation of lattice parameter on the diameter of crystal. Inaccuracy of measurements of lattice parameter was about $2 \cdot 10^{-4}$ Å.

Mechanical characteristics of crystals were evaluated by measuring of microhardness and fracture toughness K_{1C}. There was used the micromechanical method of measurement suggested by A.G.Evans and developed by V.I.Trefilov and Yu.V.Mil'man for fragile and quasi-fragile materials [5]. This method is based on the local loading of crystal by using Vickers pyramid at the chosen weight P until at the corners of print there appear cracks, and determination of ratio between sizes of plastic print (diagonal-$2d$) and length of radial cracks (c). The value of K_{1C} was defined by formula:

$$K_{1C} = (NHd^{0.5}/\Phi) \cdot (E\Phi/H)^{0.4}, \qquad (1)$$

where $H = 1854P/(2d)^2$ kg/mm^2 is the microhardness at load P in gram, $2d$ is the diagonal of print in μm, E is the Young's modulus, N is the empirically found proportionality factor which depends on the ratio (c/d), Φ — factor taking into account the roughness of surface at the opening a crack ($\Phi = 3$). The optimal value of load P was chosen in such a way that the ratio of the crack length to the size of print should be in the interval $1.7 < (c/d) < 5$ and correspond to the saturation in the function $K_{1C} = f(P)$. In our case the value of weight was $P = 250$ g. The loading was conducted automatically by using commercial hardness meter PMT-3. The surface of samples was carefully polished. The Young's modulus for magnesium aluminate spinel was taken according to paper [6] equal $E = 25.8 \cdot 10^4$ MN/м^2. The experimental inaccuracy in determination of K_{1C} was about 10 %.

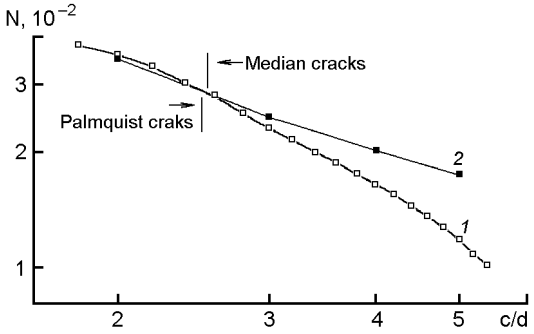

Fig. 1. Empirical dependence of $N = f(c/d)$.

For calculation of value K_{1C} the authors of paper [7] suggested the Niihara formula as optimal one in the case of Palmquist cracks creation at the indentation:

$$K_{1c} = 0.035(Hd^{0.5}/\Phi)(E\Phi/H)^{0.4}(c/d - 1)^{-0.5}, \qquad (2)$$

where $\Theta = 3$, interval of ratio $1.25 \le c/d \le 3.5$. By comparison of (1) and (2) expressions we found, that empirical dependence of $N = f(c/d)$ in chosen method is identical to Niihara dependence of $0.035(c/d - 1)^{-0.5}$ and in the given interval of $(c/d) \le 3.5$ the difference in graphs is negligible (Fig. 1). Such interval of ratio (c/d) was used in our experiment.

Magnesium aluminate spinel crystals were grown by Verneuil method at the growth rate of 5 ÷ 20 mm/h by using H_2–O_2 burner as a heating source. The composition of crystals $MgO \cdot nAl_2O_3$ was varied $n = 1.0 \div 2.5$ as for nominally pure and for doped with ions of transition metals.

The stoichiometric spinel crystals $MgO \cdot 1.0Al_2O_3$ have orientation of [100] and developed net of block structure. In Fig. 2a the tilting curve for reflection plain of (931) was taken from bulk of stoichiometric crystal, when narrow slit in collimator of 0.05 mm was used. The shape of this curve indicates the existence of two blocks with disorientation of 6′. There was found that disorientation of blocks was varied in the range from 6 to 20′. According to the blocks classification suggested in paper [8] this substructure is the third order and corresponds to sizes of blocks of 10 ÷ 100 μm. Due to the use of the narrow collimator slits it was possible to measure the

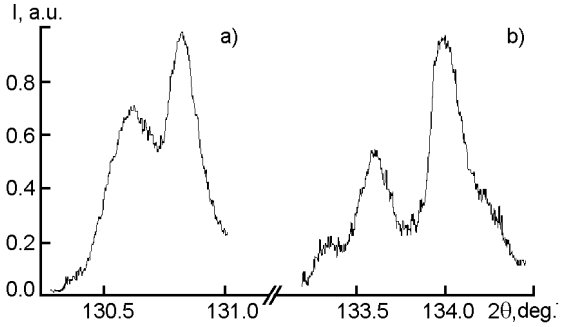

Fig. 2. The tilting curve for reflection plain of (931): $CuK_{\alpha 1}$ radiation, the width of collimator slit of 0.05 mm. (a) — stoichiometric spinel crystals, two blocks of disorientation angle of 6′. (b) — non-stoichiometric spinel crystals, three blocks of disorientation angles of 8′ and 12′.

variation of lattice parameter along of crystal radius (Table 1). It was obtained that in the center of stoichiometric crystal a = 8.0830 Å and at the periphery a = 8.0760 Å.

In Table 1 the variation of the lattice parameter and impurity concentration (in wt.%) of Fe, Cr, and Mn is presented as measured by method of fluorescent analysis with spectrometer SPRUT. Such quantitative changes of impurities along crystal radius could not be the reason of decreasing of lattice parameter. During the crystal growth the composition of crystal changes from the center to its edge. According to dependence of lattice parameter on the molar composition of crystal [9] we found the change of n = 1.0 at the center to n = 1.2 at the edge of crystal. Such decrease of lattice parameter along the crystal radius was obtained also in paper [10] and explained by displacement of access of aluminum oxide to periphery of crystal.

In our opinion such effect is related to temperature gradients of hydrogen-oxygen flame. It was obtained for studed crystals that the temperature at the axes of torch is lower to compare with that at periphery and it causes the higher evaporation of MgO at the edge of growing crystal. The sizes of powder particles are usually about 10 ÷ 40 μm. At the melting in the flame they became as much as 20 times smaller and, because of the different temperature of evaporation of magnesium and aluminum oxides, the ratio of components Al_2O_3/MgO in particles will be different in the center of torch to compare with periphery. Such melted particles of several micrometers in sizes are getting the growth zone at the surface of crystal. The growth of crystals realizes by cellular mechanism because of different stoihiometric composition particles and high rate of crystal growth. There are incoherent nucleus growing together which leads to formation dislocation boundaries and development block structure.

According to recommendation of paper [11] by choosing ratio of torch length (L) to distance from burn to melting surface (D) it is possible to regulate the temperature gradient along the radius of growing crystal. In the case $L > D$ the center of melt is washed by colder gas to compare with periphery. The temperature of center increases at small values of L/D. Therefore by variation of ratio L/D and taking into account of the temperature of muffle furnace it is possible to get the optimal condition of crystal growth at constant temperature and, consequently, the uniform composition along the radius of crystal.

As it was indicated in introduction, spinel crystals grown at high temperature conditions are partially disordered. The partially inverse structure of spinel $MgAl_2O_4$ could be written $[Mg_{1-x}Al_x](Al_{2-x}Mg_x)O_4$, i.e. the part of Mg^{2+}-ions (x, atomic fraction) in tetrahedral positions is replaced by Al^{3+}-ions, the same amount of Al^{3+}-ions in octa-positions is replaced by Mg^{2+}-ions. This leads to deformation of sizes of corresponding polyhedrons.

Table 1. Variation of lattice parameter and impurity concentration (mass.%) along radius in stoichiometric spinel crystals grown by Verneuil method

	Center	1 mm	2 mm	3 mm	4 mm	Edge
$2\theta_{max}$	130.75°	130.79°	130.80°	130.83°	130.87°	130.95°
a, Å	8.0829	8.0816	8.0812	8.0803	8.0790	8.0764
Fe	0.07	0.003	0.026	0.04	0.013	0.005
Mn	–	0.004	0.003	0.01	–	–
Cr	–	0.005	0.005	0.005	–	–

Table 2. Variation of lattice parameter and impurity concentration (mass.%) along radius in non-stoichiometric spinel crystals grown by Verneuil method

	Center	2 mm	6 mm	Edge
$2\theta_{max}$	133.32°	133.34°	133.68°	133.99°
a, °	8.0026	8.0020	7.9918	7.9826
n	2.2	2.2	2.4	2.7
Fe	–	–	–	0.005
Mn	–	–	0.024	–
Cr	–	–	0.023	–

By using experimental value of lattice parameter $a = 8.083$ Å for stoichiometric spinel crystals $n = 1$ and method suggested in paper [12] we calculated the oxygen positional parameter u, the distance cation-anion R_T in tetrahedral sites and R_O the same in octahedral sites, and also inversion parameter x:

$$u = 0.4983 \cdot a - 3.766, \quad u = 0.26176, \quad (3)$$

$$R_T = a\sqrt{3(0.125 - u)^2}, \quad R_T = 1.9147\,\text{Å}, \quad (4)$$

$$R_O = a\sqrt{(0.5 - u)^2 + 2(0.25 - u)^2}, \quad (5)$$

$$R_O = 1.93041\,\text{Å},$$

$$u = 0.2651 - 0.0123x, \quad x = 0.2715. \quad (6)$$

Non-stoichiometric spinel crystals grown from powder of composition $n = 2.5$ was also investigated. These crystals were oriented in the crystallographic direction of [110]. The lattice parameter along the radius of crystal changed from 8.0026 Å at the center to 7.9826 Å at the periphery (Table 2), which corresponds to variation in composition from $n = 2.2$ to $n = 2.7$. These crystals have also developed net of block structure with block sizes of 10 – 100 μm. In Fig. 2b the tilting curve for reflection plain of (931) is presented for non-stoichiometric spinel crystal. The shape of this curve indicates the existence of three blocks with disorientation angles of 8′ and 12′. As in a case of stoichiometric crystals the diffraction angle and lattice parameter are varied along of radius of crystal. Nevertheless, in the case of non-stoichiometric spinel crystals the changes of lattice parameter along of radius was equal $\Delta a = 0.02$ Å to compare with $\Delta a = 0.007$ Å for stoichiometric spinel.

The reason of these changes is the existence of temperature gradient in torch, and as a consequence the non-uniform evaporation of MgO as in the course of melting powder particles and also from the surface of melted layer.

The fracture toughness K_{1C} becomes a generally accepted feature of mechanical characteristics of material. The value of K_{1C} was determined by using indentation method measuring the size of diagonal of prints ($2d$) and length of radial cracks (c). These data are presented in Table 3 and were used for calculation of microhardness (H) and fracture toughness (K_{1C}).

Nominally pure spinel crystal grown by Verneuil method have the minimal value of fracture toughness $K_{1C} = 1.3$ MN/m$^{3/2}$. This value is consistent with fracture toughness calculated by using expression [13]:

$$K_{1C} = \alpha E \cdot \sqrt{\pi a}, \quad (7)$$

where parameter $\alpha = 0.1$, E is the Young's modulus, a is the lattice parameter ($a = 8.08$ Å), $K_{1C} = 1.3$ MN/m$^{3/2}$. This formula is based

Table 3. Experimental data of average diagonal of prints ($2d$), length of radial cracks (c), and calculated values of microhardness (H) and fracture toughness (K_{1C}) of crystals grown by Verneuil method

Crystal composition, doping	c, μm	d, μm	H, kg/mm^2	K_{1C}, MN/m$^{3/2}$
Stoichometric composition ($n = 1.0$)				
Nom. pure.	29.3	8.4	1632	1.3
Fe, 0.01 mass.%	22.3	7.3	2189	1.8
Mn, 0.01 mass.%	23.2	8.6	1585	1.9
Cr, 0.01 mass.%	25.5	8.4	1656	1.6
Non-stoichiometric composition				
$n = 1.5$	28	8.7	1531	1.4
$n = 2.5$; Mn	23.4	8.5	1608	1.9

Table 4. Variation of lattice parameter along radius in stoichiometric spinel crystals grown by Czochralski method

Concentration of Mn	Orientation	Angle of deviation	a, Å	
			Center	Edge
Nom. 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

on the mechanism of destruction as a sequence of breakup of inter-atomic bindings at the top of the crack.

Doping with Fe and Mn at the concentration of 0.01 mass.% leads to increasing of fracture toughness to $K_{1C} = 1.9$ MN/m$^{3/2}$, also the introduction of iron leads to the highest value of microhardness. From the precision X-ray data it was revealed that in natural spinel Fe^{2+}-ions replaces Mg^{2+} in tetrahedral positions, but Cr^{3+}-ions replaces Al^{3+} in octahedral positions [14]. We registered the high value of fracture toughness for non-stoichiomertic spinel crystals doped with manganese, which usually replaces Mg^{2+}-ions in tetrapositions.

By using Czochralski method spinel crystals were grown in iridium crucible and argon atmosphere at high frequency heating. The speed of pooling was about 1 mm/h. The nominally pure and doped with Mn to concentration of 0.02, 0.04 and 0.1 mas.% stoichiometric spinel crystals were investigated. The data on lattice parameter measured in the center and on the edge of single crystals are shown in Table 4.

The main feature of spinel crystals grown by Czochralski method is the some higher value of lattice parameter for stoichiometric crystals and the absence of block structure. As can be seen from Table 4 for nominally pure and doped with Mn to concentration of 0.02 and 0.04 mass.% the lattice parameter along of radius of crystal is constant in the limit of experimental uncertainty. The direction of crystal growth was near crystallographic direction of [310] in the range of 4 degrees. As it was indicated in paper [15], in practice, the crystals grow from melt with orientation close to tightly packed crystallographic direction with small angle of deviation.

At the doping crystal with Mn to concentration of 0.04 mass.% the deviation of crystal growth direction from orientation [310] becomes less than 1 degree, which leads to the decrease of the growth rate of crystal. For crystals doped with Mn to concentration of 0.1 mass.% the orientation of crystal growth changes to direction [100] which could be caused by influence of doping ions on the anisotropy of rate of crystal growth [16]. Also for these crystals there was observed some variation of lattice parameter from center to periphery and related to variation of doping ions concentration, which was supported by radio-luminescence data of Mn^{2+}-ions in these crystals. Because Mn^{2+}-ions in spinel crystals have preferential energy for octahedral sites equals zero they could be placed in tetrahedral and octahedral positions which leads to some redistribution of Mg^{2+}- and Al^{3+}-ions in cationic sublattice. This effect was used to produce uniform and transparent spinel ceramics by hot-pressed technology [17].

The magnesium aluminate spinel crystals with excess of magnesium containing 1.006(7) of Mg^{2+} and 1.996(4) of Al^{3+} in formula unit have the value of lattice parameter in the range $a = 8.0844$–8.0865 Å [12]. In our crystals grown by Czochralski method we obtained the average lattice parameter equals to 8.0845 Å.

In Table 5 we present the cumulative data on spinel crystals grown by Verneuil and Czochralski methods. It could be seen that in crystals grown by Czochralski method the average lattice parameter is

Table 5. Structural parameters of spinel crystals grown by Verneuil and Czochralski methods

Crystals	a, Å	u	R_T, Å	R_O, Å	x
Verneuil	8.0829	0.2618	1.9147	1.9304	0.27
Czochralski	8.0845	0.2625	1.9254	1.9254	0.21

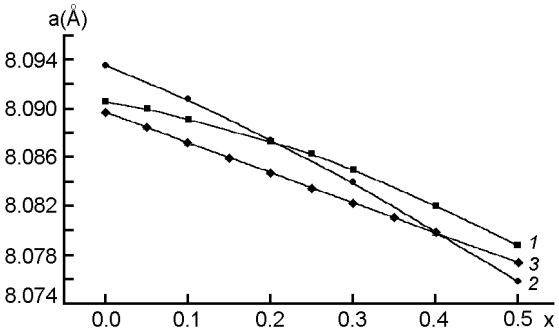

Fig. 3. Dependencies of lattice parameter on the inversion parameter magnesium spinel for different crysallo-chemical models: *1* – P.Pua model; *2* – P.Pua model corrected (for radius of cations); *3* – Calculated according to formula (9)

higher and inversion parameter lower to compare with that of Verneuil grown crystals.

To explain this data we analyze the dependences of lattice parameters on the inverse parameter for magnesium aluminate spinel crystals. In Fig. 3 we presented the dependencies of lattice parameter on the inversion parameter for magnesium aluminate spinel crystals according to crystal-chemical model of *P.* Pua [18], which could be written

$$a = 2.0995 \cdot R_T + \\ + (5.8182 \cdot R_O^2 - 1.4107 R_T^2)^{1/2}, \quad (8)$$

where R_T was taken as $R_T(\mathrm{Mg}) = 1.984$ Å and $R_T(\mathrm{Al}) = 1.765$ Å for Mg and Al ions in tetrahedral sites, and R_O equals to $R_O(\mathrm{Mg}) = 2.106$ Å and $R_O(\mathrm{Al}) = 1.898$ Å for Mg and Al ions in octahedral sites. For normal spinel structure according to P.Pua model the lattice parameter is equal $a = 8.09$ Å and dependence a on the inversion parameter is shown in Fig. 3.

Using the latest data [12] for cation-anion distances $R_T(\mathrm{Mg}) = 1.966$ Å and $R_T(\mathrm{Al}) = 1.774$ Å for Mg and Al ions in tetrahedral sites, and R_O equals to $R_O(\mathrm{Mg}) = 2.081$ Å and $R_O(\mathrm{Al}) = 1.908$ Å for Mg and Al ions in octahedral sites this value was calculated to be $a = 8.0935$ Å.

By using expression (3) and (6) we can obtain the linear dependence $a = f(x)$:

$$a = 8.0897 - 0.02468x, \quad (9)$$

where value 8.0897 Å corresponds to normal structure of magnesium aluminate spinel ($x = 0$). The dependence of lattice parameter on the inversion parameter as straight line is also shown in Fig. 3.

Therefore, there are two origins for higher value of lattice parameter in nominally pure stoichiometric spinel crystals grown by Czochralski method: (a) the excess of Mg^{2+}-cations in elementary cell and decreasing of inversion parameter x.

The fracture toughness was measured as for nominally pure so for Mn doped spinel crystals grown by Czochralski method. The averaged data are presented in Table 6. Czochralski grown spinel crystals have higher values of microhardness and fracture toughness to compare with that of crystals, grown by Verneuil method. This could be explained by the absence of blocks in specimens and more perfect structure at atomic level, particularly, the lower degree of inversion.

Our data on the fracture toughness of spinel crystals grown by Verneuil method are consistent with measured K_{1C} for different planes of single crystals (100), (110), and (111) which was equal to 1.18, 1.54 and 1.90 MN/m$^{3/2}$, respectively [19]. Data for nominally pure spinel crystals $K_{1C} =$ 1.30 MN/m$^{3/2}$ are somewhat average value of fracture toughness, but for crystal doped with Mn the value $K_{1C} = 1.90$ MN/m$^{3/2}$ coincide with that for (111) plane. To explain the much higher values of fracture toughness in Czochralski grown spinel crystals we need to provide further investigations.

Thus, in the magnesium aluminate spinel crystals grown by Verneuil methods there was observed the variation of composition from center to periphery of crystal which

Table 6. Fracture toughness of stoichiometric magnesium aluminate spinel crystals grown by Czochralski method

Concentration Mn, mass. %	c, μm	d, μm	H, kg/mm^2	K_{1C}, MN/m$^{3/2}$
Nominally pure	18.8	7.8	1914	2.5
0.02	17.7	7.6	2019	2.7
0.04	15.8	7.9	1845	2.8

caused by non-uniform evaporation of MgO from the surface of melted particles of powder and from the thing film of melt at the surface of growing crystal. This effect could be due changes of radial temperature in the torch of furnace of crystallization. Micro blocks in these crystals are formed due to cellular growth caused by instability of crystallization front, by the high rate of crystal growth, and by non-uniform distribution of magnesium along of radius of growing crystal. The magnesium aluminate spinel crystals grown by Czochralski method have more perfect structure. The micro blocks in these crystals are absent and composition of crystals is constant along of radius. The fracture toughness measured by using indentation method of nominally pure Verneuil grown spinel crystals is equal to $K_{1c} = 1.3$ MN/m$^{3/2}$. Doping of these crystals with transition metals ions of Mn and Fe to concentration of 0.01 wt.% leads to the higher resistance to the crack development in doped crystals. The fracture toughness of spinel crystals grown by Czochralski method has much higher values of $K_{1C} = 2.5 \div 2.8$ MN/m$^{3/2}$.

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Структурні та механічні характеристики кристалів магній-алюмінієвої шпінелі, вирощених методами Вернейля та Чохральського

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Проведено рентгенівські дифракційні дослідження кристалів магній-алюмінієвої шпінелі стехіометричного та нестехіометричного складу, вирощених методом Вернейля. Знайдено зменшення вмісту MgO на периферії кристалів порівняно з його центром. Знайдено блочну структуру цих кристалів та обговорюються умови її створення. Досліджені кристали шпінелі, вирощені методом Чохральського, як номінально чисті, так і активовані іонами марганцю до концентрацій 0,02, 0,04, та 0,1 мас%. Спостерігалася відсутність зміни складу вздовж радіуса кристалів. Більш високі механічні характеристики отримано для кристалів, вирощених методом Чохральського.