

# ACTIVATED FORSTERITE CRYSTAL GROWTH.

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## ABSTRACT.

Forsterite crystals, doped with  $\text{Cr}^{4+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{V}^{4+}$ , were grown by Czochralski technique. Dependence of ionic valence condition and crystal generation characteristics upon ambient of growth is showed. It's elicited that  $\text{Mg}_2\text{SiO}_4:\text{Cr}^{4+}$  growth demands creation of specified conditions preventing  $\text{Cr}^{2+}$  formation (absorption band of  $\text{Cr}^{2+}$  lies in oscillation region of  $\text{Cr}^{4+}$ ). Absorption spectrum of above enumerated ions in Forsterite structure is examined.

## 1.Introduction.

In connection with ability to pun on dn-configuration ions isomorphic in the Forsterite structure, this type of crystals is of the great interest as active medium for tunable lasers.  $\text{Mg}_2\text{SiO}_4$  crystal growth and properties investigation were reported in a number of works [1,2].

This work is devoted to growing of Forsterite crystals doped with  $\text{Cr}^{4+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{V}^{4+}$ . Also we have studied some properties of these matrixes.

First the crystalline stricture of Forsterite was studied by Bragg and Brown [3]. The main structure motive is created by oxygen atoms and represent the closest atomic packing which is very similar to hexagonal one. A part of distorted octaedral voids is occupied with magnesium atoms. Silicon atoms take up a little bit distorted tetrahedral voids as well. The structure is close to spinel structure. There are two kinds of crystallographically non-equivalent magnesium atoms. Some of them are situated in inversion centers (point symmetry  $C_i$ ), the rest is in principle planes (point symmetry  $C_s$ ). Forsterite crystallizes in rhombic syngony. Spatial group -  $\text{Pbnm}(D_{2h}^{16})$ .

## **2. Experimental part.**

Charge was preparing from MgO and SiO<sub>2</sub> oxides ceramic technique. Investigation of solid phase Mg<sub>2</sub>SiO<sub>4</sub> formation kinetics showed that there was no 100% conversion of the started oxides to Forsterite if the temperature was equal to 1200°C and time delay lasted 70 hours. X-ray phase analysis discovered in refraction products MgO, SiO<sub>2</sub>, Mg<sub>2</sub>SiO<sub>4</sub> and MgSiO<sub>3</sub> (enstatite). Complete Forsterite synthesis took place when the charge was melting.

Forsterite crystals were grown from by Czochralski technique iridium crucibles in neutral, oxidizing and reducing mediums. Gas medium depended from physical-chemical characteristics of ions-activators. Pulling rate and rotation rate varied depending on experiment objective and had values:  $V = 1-2\text{mm/hr}$  and  $\omega = 15-60\text{rev/min}$ .

For high quality crystals obtaining pulling rate is reduced to 1mm/hr. Rotation rate depends on crucible diameter and crystal diameter ratio. Temperature gradients, produced in heat assembly, influence on rotation rate also. After the end of growing process obtained crystals were cooled with the rate of 70-150°C/hr. Temperature gradients measured by tungsten-rhenium thermocouples had values of: axial – 15-30°C/cm, radial – 10-20°C/cm.

During Forsterite growing process incongruent dissociation of the melt took place. It caused break of melt stoichiometry and extrinsic phases formation. They differed in color from the melt bulk which had been crystallized in crucible. When the growth process run in reducing medium, formation of rhombic-shaped enstatite took place in the crucible center whereas there was clinoenstatite of monocline syngony on each side of a crucible. This fact was discovered by X-ray phase analysis. Pulling crystal can capture extraneous phases and it considerably decrease the quality.

Formation of the mentioned phases connects with the absence of 100% transformation of the starting oxides to Forsterite during fore synthesis in the open air with the temperature of 1200°C. High volatility of unbound (free, combined) MgO in reducing medium with the temperature 1800°C is observed [4], that's why there was melt non-stoichiometry with the lack of MgO when a crucible with charge was rapidly heated.

During Mg<sub>2</sub>SiO<sub>4</sub> growth we marked thermal etching starting from the length of 10-15mm. We accounted it for MgO evaporation and corrected the melt by MgO excess.

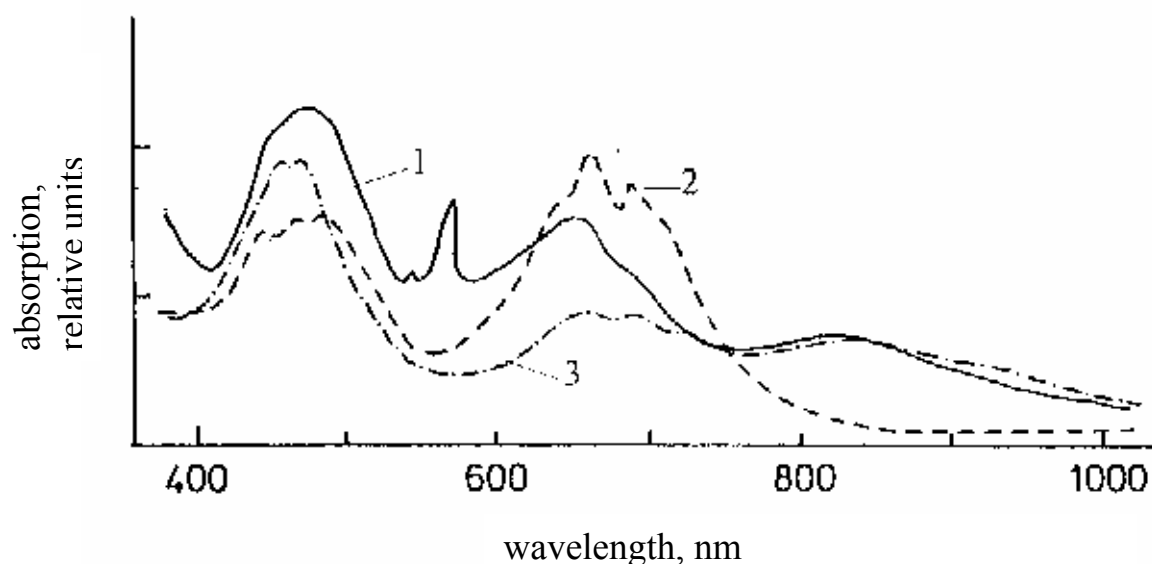
Though thermal etching of crystal surface didn't cease and optical quality lowered greatly. We managed to prevent crystal thermal etching by adding SiO<sub>2</sub> excess to the melt. Quantity of SiO<sub>2</sub> was in dependence on valence and quantity of ion-activator and on thermal SiO<sub>2</sub> dissociation speed under the crystallization temperature.

Identification of valence and coordination state of impurity ions in Forsterite lattice was realized by analysis of optical absorption polarization centers. In a number of difficult cases we also analyzed EPR spectrum data.

Absorption spectrums were recorded on bi-rays spectrophotometers CΦ-8 (Russia) and Hitachi-VIS12 (Japan) and were analyzed by PC-100.

### **3. Results and discussions.**

Several peaks, caused by chromium ions of different valence (Cr<sup>4+</sup>, Cr<sup>3+</sup>, Cr<sup>2+</sup>) were observed during Cr-doped Mg<sub>2</sub>SiO<sub>4</sub> crystal growth in argon atmosphere (fig.1).



*Figure 1. Absorption spectrums of Cr-doped Forsterite crystals grown in neutral ambient. 1. E//a; 2. E//c; 3. E//b.*

In Forsterite structure Mg ions are replaced by  $\text{Cr}^{2+}$  and  $\text{Cr}^{3+}$  ions in octahedral positions and  $\text{Cr}^{4+}$  ions deputize for  $\text{Si}^{4+}$  in tetrahedral positions.

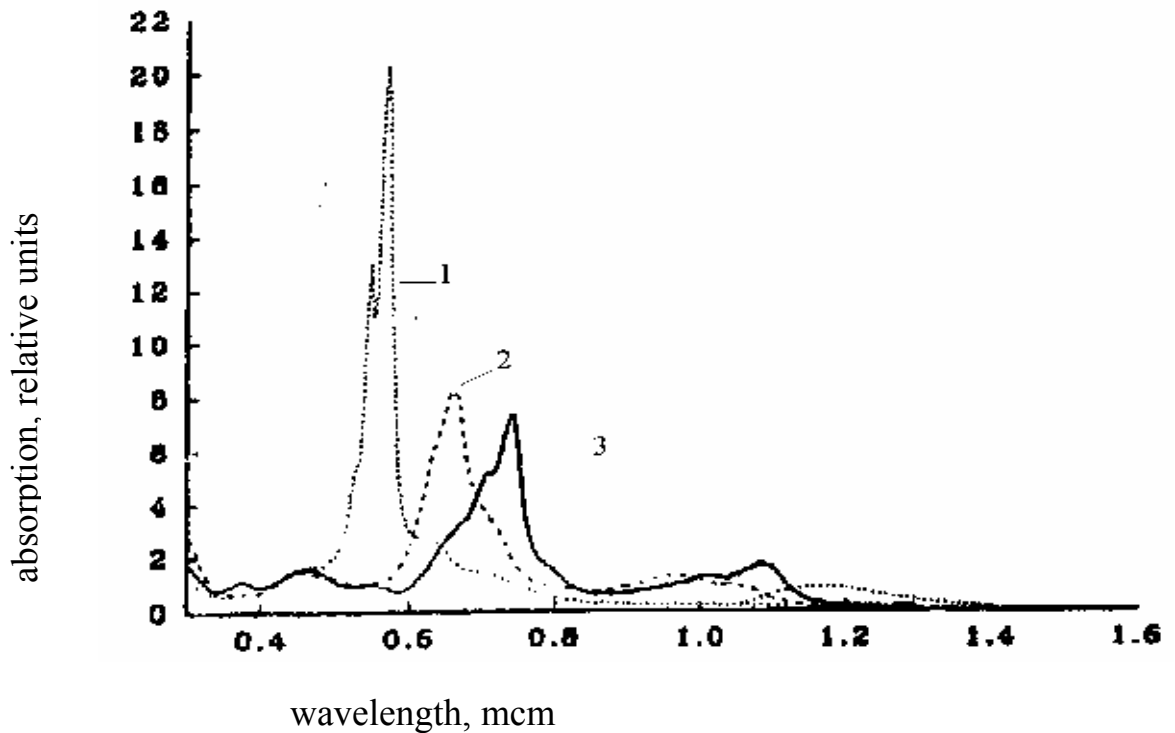
Figure 1 shows absorption spectrums measured in polarized light at room temperature. They have two broad stripes which correspond to transitions  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ ,  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$  with maximums in regions 660nm and 469nm [5]. These peaks belong to  $\text{Cr}^{3+}$  ion. Besides these main strips there are two narrow strips with maximums 550nm and 570nm in spectrum measured when E//a. Narrow strips can be correlated with  ${}^4\text{A}_2 \rightarrow {}^2\text{T}_2$  transition. They pertain to  $\text{Cr}^{3+}$  in other octahedral position. During polarization E//b and E//a a broad strip with maximum at 860nm can be seen. On the spectrum in polarization E//b small peak with maximum 730nm related to  $\text{Cr}^{4+}$  can be noticed.

Depending on setting task it's possible to manage purposefully Cr ions' valence and therefore as well as absorption spectrum peaks. It can be done by dispose them of some ones and by enlarging amplitude of others with the help of atmosphere composition alteration in growth chamber.

So, growing crystals in oxidizing atmosphere we can completely get rid of peak  $\text{Cr}^{2+}$  at  $\lambda = 860\text{nm}$  and increase peak  $\text{Cr}^{4+}$  at  $\lambda = 1100\text{nm}$ . It provides effective crystal pumping at  $\lambda = 1060\text{nm}$ . Apart from it,  $\text{Cr}^{4+}$  peak intensity at  $\lambda = 730\text{nm}$  rises also and its open the possibility to pump this medium by diodes at  $\lambda = 810\text{nm}$ , which are well assimilated.

Absorption spectrums of Cr-doped Forsterite grown in oxidizing atmosphere are given on Figure 2.

If it's necessary to obtain intensive  $\text{Cr}^{2+}$  absorption peaks at  $\lambda = 860\text{nm}$  and 1800nm Forsterite crystals must be grown in reducing medium. Absorption spectrums of such crystals are showed on Figure 3. Out of this we can assert that such crystal can be effectively pumped by diode at  $\lambda = 850\text{nm}$  as well as pumped in band of 1800nm with the help of available sources. As appears from the below given Fig.3 it's impossible to obtain effective optical generation on  $\text{Cr}^{4+}$  ions if a crystal has  $\text{Cr}^{2+}$ . It can be explained by broad  $\text{Cr}^{2+}$  absorption band which lies in their generation band of 1167-1345nm. So it's extremely important to prevent  $\text{Cr}^{2+}$  formation when growing in oxidizing atmosphere in order to obtain high-efficiency laser crystals on  $\text{Cr}^{4+}$  ions.

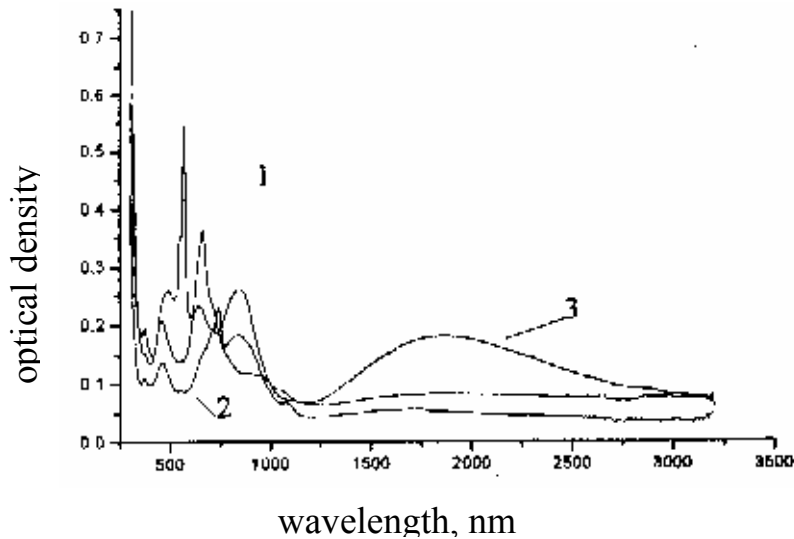


*Fig.2 Absorption spectrums of Cr-doped Forsterite grown in oxidizing atmosphere. 1. E//a; 2. E//c; 3. E//b.*

Also we obtained Forsterite crystals doped by  $V^{4+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$  ions. Assignment of absorption bands to electron levels of impurity ions which are form a part of Forsterite lattice (as well as chromium does) in different valence states in octahedral and tetrahedral positions demands for more careful analysis.

Spectroscopic properties of vanadium ions in Forsterite were studied detail in the works [6], [7], [8]. So we should focus an attention on the fact that absorption spectrum belongs to demonstration of spectroscopic properties of  $V^{4+}$  tetrahedrally coordinated ions (Fig.4). Transitions from primary  ${}^2E$  state to excited  ${}^2T_2$  state have maximums in 500-1250 regions (depending on radiation polarization). It match good to the selection rules for transition between vanadium ions levels in tetrahedral surroundings with Cs local symmetry. Weak absorption stripe in 428nm region in -c

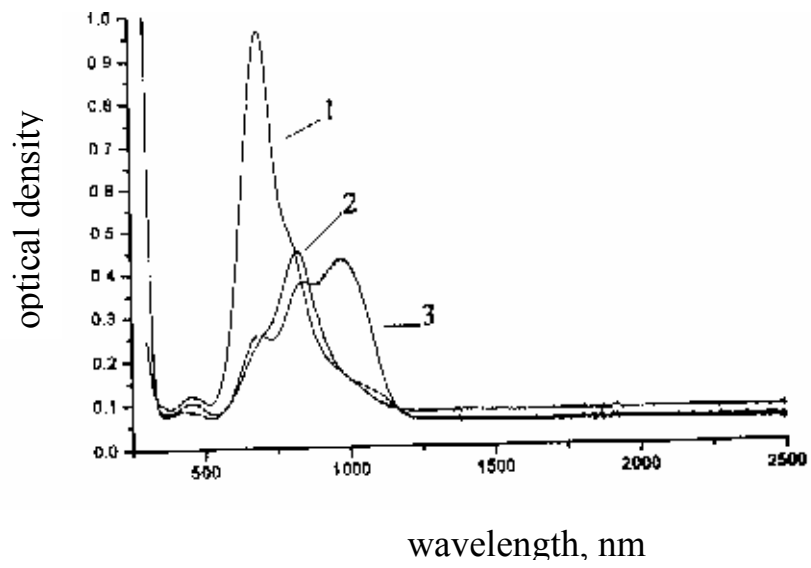
polarization and in 460nm region in  $-b$  polarization can be referred to transitions between  $V^{3+}$  octahedrally coordinated ions. Luminescent spectrum investigation revealed that radiation process on  $V^{4+}$  transitions was strongly suppressed by nonradiative relaxation through phonon subsystem.



*Fig.3. Absorption spectrums of Cr-activated Forsterite grown in reducing atmosphere. 1. E//a; 2. E//b; 3. E//c.*

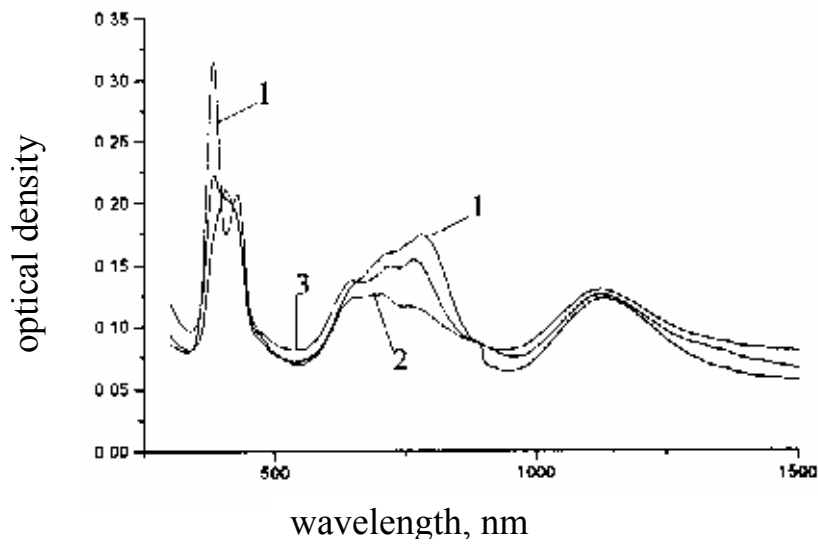
Absorption spectrum of nickel ions in Forsterite is connected with bivalent ions that are located in octahedral surrounding (Fig.5). Three strong absorption spectral lines (linked with transitions  ${}^3A_2 \rightarrow {}^3T_1(F)$ ,  $1A_2 \rightarrow {}^3T_1(F)$ ,  ${}^3A_2 \rightarrow {}^3T_1(P)$  in regions 1000-1250 nm, 625-870nm and 400-500nm) have polarization dependence which is typical for bivalent nickel with  $C_s$  local symmetry. Crystalline field parameter for the given  $Ni^{2+}$  ion configuration amounts to  $Dq = 875\text{cm}^{-1}$  when  $B = 950\text{cm}^{-1}$ .

Nickel ions' luminescence in Forsterite was studied in nearest IR-range when exciting in  ${}^3T_2$  line. Its strong temperature suppressing was observed at room temperature. Ratio of radiation intensities at transition  ${}^3T_2(F) \rightarrow {}^3A_2$  at liquid nitrogen temperature and room temperature was equal to  $\sim 30$ . Luminescence line contour for 77K was composed of sharp O-phonon line at 1375 nm and of nonstructure vibronic line in region 1400-1700 nm with maximum at 1500 nm.



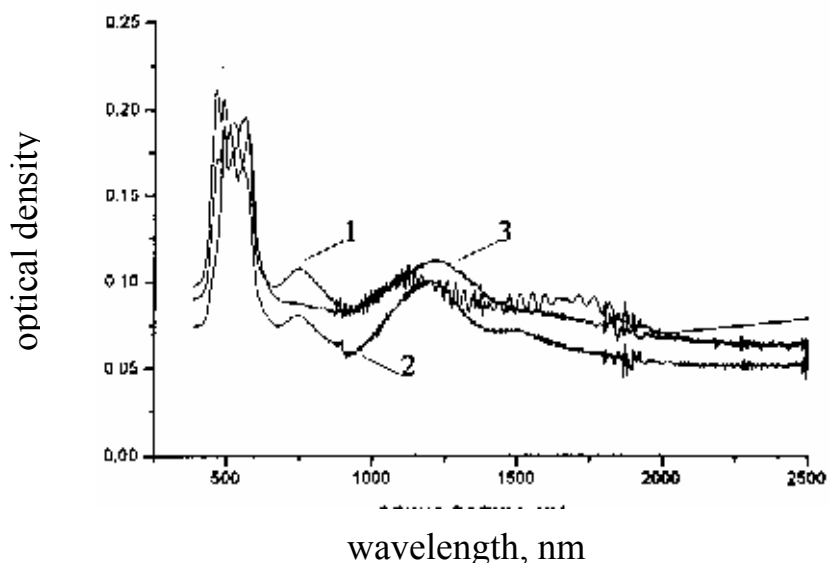
*Figure 4. "Absorption spectrums of forsterite doped with vanadium ions"*

*1. E//a; 2. E//b; 3.E//c.*



*Figure 5. Absorption spectrum of Forsterite, activated with Nickel*

*ions.1. E//a; 2. E//b; 3. E//c.*



*Figure 6. Absorption spectrum of Forsterite, activated with Cobalt ions.*

*1. E//b; 2. E//a; 3. E//c.*

Absorption spectrum of cobalt ions in Forsterite structure has the typical shape for bivalent ions in octahedral surrounding (Fig. 6). There are two main absorption regions, which are connected with  ${}^4T_1(F) \rightarrow {}^4T_2$  in the nearest IR-range of the spectrum – 1000nm-1250nm and  ${}^4T_1(F) \rightarrow {}^4T_1(P)$  – in visible one about 500nm. Transition in visible region has high intensity typical for octahedrally coordinated cobalt ions. This intensity more than two times exceeds other allowed transition. There is a weak absorption line in polarizations a and b in 750nm-region of absorption spectrum. This line is linked with  ${}^4T_2 \rightarrow {}^4A_2$  transition which is characteristic of octahedral coordination of bivalent ion.

Study of luminescence properties was accomplished at room temperature. Ionic excitation for  ${}^4T_1(P)$  level was realized by radiation having 488nm wavelength. Obtained luminescence spectrum is identified with vibronic transitions between  ${}^4T_2 \rightarrow {}^4T_1(F)$  levels in 1200-1280nm region with maximum at 2000nm and between  ${}^4T_1(P) \rightarrow {}^4T_2$  levels in 700-1100 region. Today spectral-kinetic parameters of ionic luminescence are being defined more precisely. According to preliminary analysis

data we can count  ${}^4T_2 \rightarrow {}^4T_1(F)$  transition as very prospective for obtaining generation of stimulated radiation in 2000-3000nm range.

#### **4. Conclusion**

In this work Cr valence state in Forsterite structure dependence from the atmosphere of growth is showed. It gives an opportunity to manage Cr valence purposefully as well as to obtain crystals with necessary characteristics.

$Mg_2SiO_4:Cr^{4+}$  crystal growth demands sufficient oxidizing conditions in order to minimize formation  $Cr^{2+}$  ions, which absorption band lies in  $Cr^{4+}$  generation region, that reduce efficiency power of  $Cr^{4+}$  lasers.

$Cr^{2+}$  absorption band in 1800 nm region is of the great interest for obtaining middle-IR range generation. Moreover, the band at 860 nm allow to use diode pumping on  $\lambda = 850$  nm.

In order to prevent enstatite formation and to improve optical quality, charge synthesis should be implemented up to complete transformation of starting chemicals to Forsterite crystal.

The accomplished research works resulted in great improvement of optical quality of Forsterite crystals and also in optical elements' FOM increasing ( $FOM = \alpha_{\text{absorption } \lambda = 1060 \text{ nm}} / \alpha_{\text{absorption } \lambda = 125 \text{ nm}}$ ) from 50 to 200.

## **Literature.**

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## **Summary.**

$\text{Cr}^{4+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{V}^{4+}$  - doped samples of Forsterite were grown by Czochralski technique. Ionic valence condition and crystal oscillation characteristics were found to depend on growth ambient. Absorption spectra of above-listed ions in Forsterite structure was studied. Prospective use of doped Forsterite crystal is showed in tunable lasers field.