

# CRYSTALS FOR TUNABLE LASERS OF NEAREST IR-RANGE

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Compounds, what crystallize in BeO-Al<sub>2</sub>O<sub>3</sub>-system, doped by transition metal ions, in general of iron group, are considered in this work. Spectrum characteristics and information about the crystals' quality are displayed.

## Introduction.

Compounds are formed in BeO-Al<sub>2</sub>O<sub>3</sub>-system (Fig. 1), their atoms except BeO can be changed isomorphically by transition metal ions, such as Cr<sup>3+</sup>, Ti<sup>3+</sup>, Ni<sup>2+</sup>, in what tunable lasers are interested in. Compounds from this system such as Alexandrite (BeAl<sub>2</sub>O<sub>4</sub>:Cr<sup>3+</sup>) and Al<sub>2</sub>O<sub>3</sub>:Ti<sup>3+</sup> have been studied already enough, therefore only new data will be given here. Single article about beryllium hexa-aluminate BeAl<sub>6</sub>O<sub>10</sub> was published (Matrosov V.N. et al., 1986), and one work about getting of Be<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> compound is known (Matrosov V.N. et al., 1998).

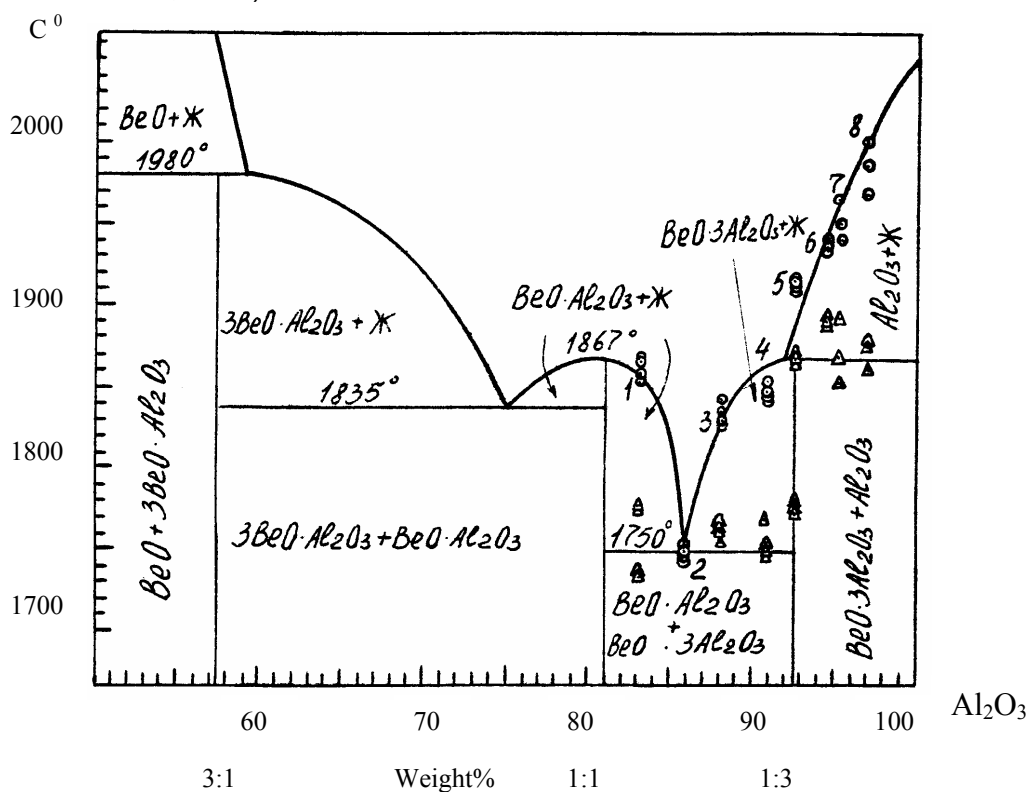


Fig 1. Diagram of states for BeO-Al<sub>2</sub>O<sub>3</sub>. (Matrosov V.N. et al., 1986)

## Aim of work.

Growing conditions research and properties of doped crystals, what form in BeO-Al<sub>2</sub>O<sub>3</sub> – system.

### Obtained results.

For growing of all crystals the charge was used what was got by ceramic way from the oxides. Charge synthesis was realized in resistive furnace at 1100°C. Keeping time was not over 20 hours. All crystals were got by Czochralsky technique from iridium and molybdenum crucibles in High Frequency Pullers.

Several problems rise during the growing of  $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$  crystals, they influence essentially on crystals quality and their spectrum-oscillation characteristics. One of them is connected with thermal dissociation of  $\text{Al}_2\text{O}_3$  at high temperature. Others – with reactions are caused by physical-chemical interaction of the melt and dissociation products with the crucible's material and atmosphere of growing. Weight-spectrum analysis demonstrated  $\text{O}^+$ ,  $\text{O}_2^+$ ,  $\text{Al}^+$ ,  $\text{AlO}_2^+$ ,  $\text{Al}_2\text{O}_2^+$  (Richard P. Et al., 1964; Semiletov S.A. et al., 1968) as the dissociation's products. The dissociation's products of aluminum oxide, having the high steam density, create gas inclusions in the melt, what, accumulating at the crystallization front, can be caught by the growing crystal. Moreover, dissociation directs to the break of stoichiometry and deformation of crystal lattice. All of this reduces crystals optical quality and their damage threshold.

Oxygen what was evolved from heating scheme materials, charge and as a result of  $\text{Al}_2\text{O}_3$  decomposition interacts with crucible's material, for instance, molybdenum to oxide it. Weight-spectrum analysis found  $\text{MoO}$ ,  $\text{MoO}_2$ ,  $\text{MoO}_3$  (Semiletov S.A. et al., 1968). These composition can decompose to Mo what, building into crystal, reduces its damage threshold and increases wave front distortion.

Working on the task of  $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$  crystal growing for terra-watt f-second amplifier (rod's diameter = 35 mm) we are faced with problem of centre's defect in big size crystals, non-uniform  $\text{Ti}^{3+}$  - distribution on diameter and with big wave front distortion what appears due to high radial temperature gradients in crystal.

As result of conducted experiments we turned out well to minimum all mentioned above defects and obtain  $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$  crystals. They were used with success in terra-watt amplifiers.

Laser rods specification is the following:

Size:  $\varnothing$  35\*15 mm. Absorption coefficient - @ 532 nm  $\alpha_{532} = 2 \text{ cm}^{-1}$ . F.O.M. ( $\alpha_{490}/\alpha_{800}$ ) = 150-200. Wave front distortion -  $\lambda/10$ , ( $\lambda = 633 \text{ nm}$ ). Unhomogeneity of  $\text{Ti}^{3+}$  - distribution along the rod's diameter – 4%.

Firstly we grew Alexandrite crystals in 1974. First article about getting of optical oscillation was published in 1978 and stimulated great search of new laser materials Cr – ions doped (Bukin G.V. et al., 1978). Alexandrite crystals could not find putting into operation due to the low optical quality long time.

Defects in Alexandrite crystals were investigated by chemical etch method, XR – topography, Eelectronic and optical microscopy.

As selective etching we used the compounds of  $\text{K}_2\text{S}_2\text{O}_7$  and KOH. The  $\text{K}_2\text{S}_2\text{O}_7$  compound allowed to identify small holes on surfaces (100) and (010), and KOH on (100) and (001).

“Sylvania Electric Products” procedure was used to count dislocations' concentration. The dislocations' concentration was  $n (10^2\div 10^3) \text{ cm}^{-2}$  in Alexandrite crystals.

Direct dislocations' observation in Alexandrite crystals was realized by XR diffraction topography method (Lang method). Obtained results confirmed that practically all defects (including dislocations) of seed are succeeded to crystal in these or that case. And most dangerous for crystals those dislocation what oriented in parallel or sub-parallel with its growing direction. They penetrate into crystal and, in many cases, distribute along its length. Another source of dislocations' formation is momentary melt crystallization at the seed during inserting it into the melt. And big quantity of dislocations' formation is

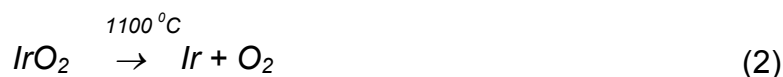
connected with not only extreme quickness of crystal structure building, but with plentiful of micro-bubbles what are the source of additional dislocations. One circumstance pays attention that observed dislocations were at the periphery or as mixture with predominance of periphery component in crystals [100] and [010] oriented, and as spiral in crystals [001] oriented. It needs to say, that due to anisotropy of the melt wet of the seed, lifting of the melt on the seed thanks to surface tension forces that occurs only at sides {010} and {001}. Therefore parts of the crystal localized only from these sides with high dislocation's density.

Inclusions of foreign phases are the active source of dislocations. The volumes of tensions near these inclusions can be over tens percents from average in the crystal. Therefore the palaces of such tension's concentration are favorable for origin and duplicating of dislocations.

Research of the reasons of dislocation arising allowed to us to work out the crystal growing technology with minimum dislocation's density.

It was shown experimentally that when dislocation density reaches some level in the crystal, a field of mechanical tension, what arises from them, leads to the great birefringence and can lead to the polarization. Therefore, dislocations are one of the main sources of crystals' optical heterogeneity. Due to the Cr-distribution coefficient is more than one, we observed its striation distribution along the crystal length during the crystal growing. Three types of striation were observed. The first one was crude aperiodic with a distance between bands more than 150  $\mu\text{m}$ . This type of birefringence arises due to fluctuation of the melt temperature at the front crystallization or during the forming of inclined sides {111} on the side faces. Cr-concentration can be more in several times in such band than in main crystal volume, that leads to changing of refraction coefficient and to the declining of its laser characteristics. To avoid this striation it is possible by reduction of temperature fluctuations of the melt thanks to decreasing of power supply vibrations of the source of crucible heating. The second type of striation is periodical, it occurs due to disalignment of crystal axis with heat crucible axis. Its periodicity depends on the rotation speed of crystal and equal  $\approx 40\text{-}60 \mu\text{m}$ . Cr-concentration is much lower in these bands than in the first type. The third type of striation is periodical as well and is connected with vibrations of the melt temperature due to convection flues in crucible. Approximate bands' period is 10  $\mu\text{m}$ . Cr-concentration is much lower in these bands than in the second type, and these bands do not influent essentially on the laser characteristics of crystal. Technical methods allow to reduce the first and the second types of striation. It is very difficult to direct the third type of striation due to temperature gradients, and it means convection, are in the melt every time.

Inclusions of small-dispersion iridium create big problems in Alexandrite crystals. They are formed due to oxidize of iridium crucible. Oxidize surrounding is brought about by thermal dissociation of the melt, low level of vacuum in the chamber, oxygen's residue what is brought with the charge and ceramic. Reaction of formation of small-dispersion iridium runs in two stages.



Compact iridium, from what crucible consists, is oxidized to  $\text{IrO}_2$  (equation 1) at the first stage. Then formatted oxide  $\text{IrO}_2$  is decomposed to small-dispersion iridium and oxygen (equation 2). This iridium is captured by the grown crystal sharply down its optical quality and volume of beam strength. The flow of protection gas through the chamber

during the crystal growing process is effective method of fight against inclusions. It allows to remove iridium oxide before its decomposition to iridium and oxygen and to make better the optical quality of crystals.

Alexandrite crystals have tendency to creation of sliding planes. It arises when radial temperature gradients during crystal growing are more than  $50^{\circ}\text{C}/\text{cm}$ . Mechanical strength is run between internal and external volumes of crystal what leads to formation of sliding planes, as a rule, along with planes of absolute seal of crystal. The sliding planes can be a place of arising of dislocations, and can initiate volume break-downs during interaction with laser oscillation. Therefore it is very important controlling of radial gradients do not exceed  $50^{\circ}\text{C}/\text{cm}$  during the Alexandrite crystal growing.

Works for development of Alexandrite lasers with diode pumping have been activated last time. We grew samples for it with Cr-concentration 0,5 at% ( $\alpha_{595\text{ nm}} = 24,0\text{ cm}^{-1}$ ), with absorption coefficient at oscillation wave length  $\alpha_{750\text{ nm}} = 0,001\text{ cm}^{-1}$  without inclusions of iridium and passed them for the conducting of investigations.

Firstly we grew beryllium hexa-aluminate ( $\text{BeAl}_6\text{O}_{10}$ ) crystals  $\text{Cr}^{3+}$  and  $\text{Ti}^{3+}$  doped in 1984. Micro-bubbles were the main crystal defect. Some spectroscopy characteristics of this compound are brought in the Table. Crystals fall in ortho rhombic syngony and are bi-axis. Refractive indexes at  $\lambda=0,7\text{ }\mu\text{m}$   $\text{Na}=1,737$ ;  $\text{Nb}=1,740$ ;  $\text{Nc}=1,735$ . Nonlinear refractive index  $T=1,37\cdot 10^{-13}$ . Transmission is from  $40000\text{ cm}^{-1}$  to  $2000\text{ cm}^{-1}$ . Density –  $3,74\text{ gm}/\text{cm}^3$ . Heat conduction –  $12,5\text{ W}/\text{m }^{\circ}\text{C}$ . Coefficient of thermal expansion  $\alpha=6,78\cdot 10^{-6}\text{ K}^{-1}$ .

We firstly realized optical oscillation on  $\text{BeAl}_6\text{O}_{10}:\text{Cr}^{3+}$  crystals (Alimpiev A.I. et al., 1988). Absorption and luminescence spectra shown on Fig. 2 and 3. As it is seen from absorption spectra diodes can be successfully used for pumping of this medium, and as  $\tau_{\text{LYM}}=13,5\text{ }\mu\text{m}$  the medium can be pumped by lamps. Tunable oscillation was obtained for coherent at  $\lambda = 532\text{ nm}$  and lamp pumping. Laser rod sized  $\varnothing 3 * 25\text{ mm}$  and lamp INP-2 with the length of discharge distance =  $45\text{ mm}$  were used for experiments. Threshold was  $10\text{ J}$  for free oscillation mode. Tunable range was  $780\div 920\text{ nm}$ . The width of oscillation spectra was  $\approx 1\text{ nm}$  in maximum of band at  $830\text{ nm}$  (Pestriakov E.V. et al., 1993). Experiments indicated that tunable range can be made wider over  $1000\text{ nm}$ . Such way new medium is very prospective for using in tunable lasers.

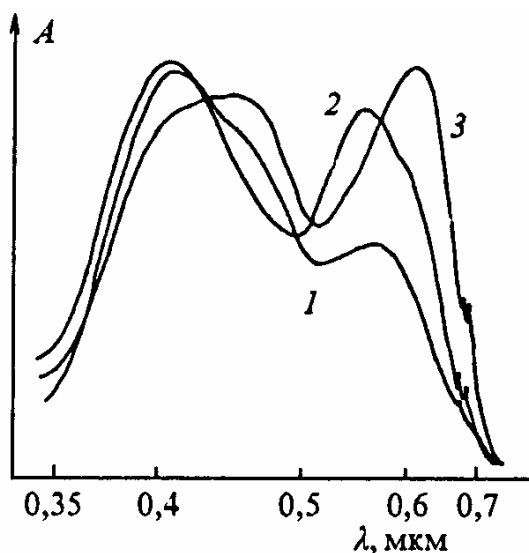


Fig 2. Absorption spectra  $\text{BeAl}_6\text{O}_{10}:\text{Cr}^{3+}$  for  $E//c$  (1),  $E//b$  (2) and  $E//c$  (3).

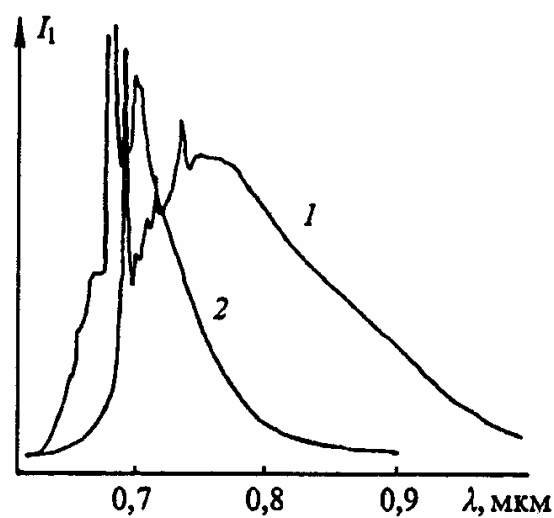


Fig 3. Luminescence spectra  $\text{Cr}^{3+}$  in  $\text{BeAl}_6\text{O}_{10}$  (1) and  $\text{BeAl}_2\text{O}_4$  (2).

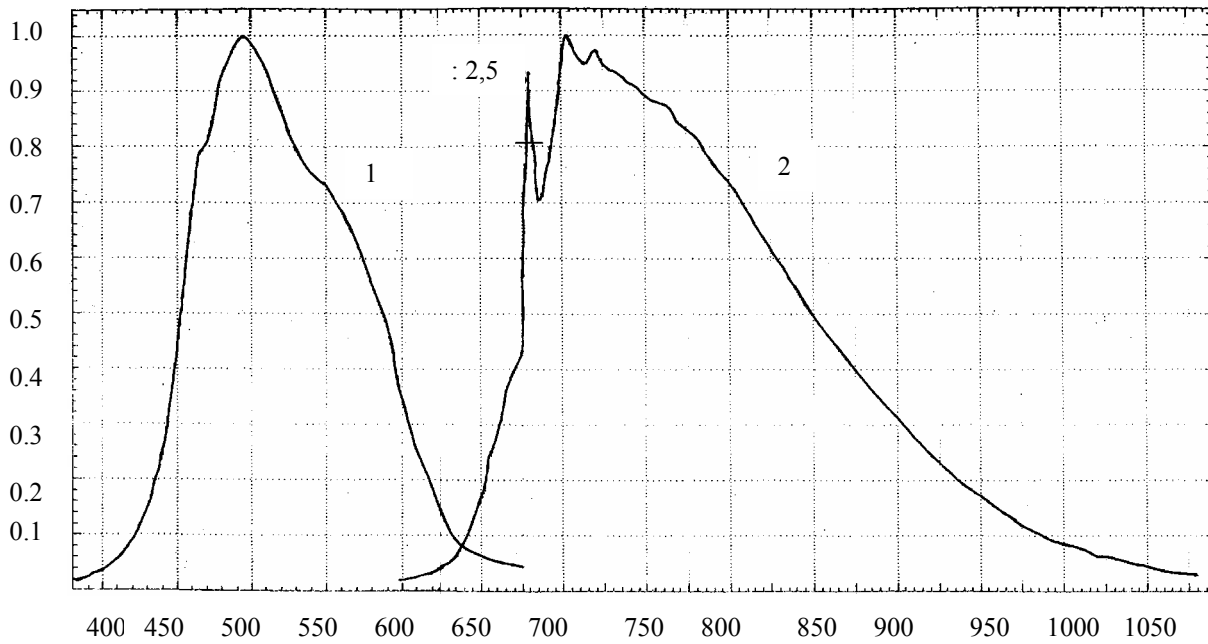
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Fig 4. Absorption (1) and oscillation (2) spectra  $\text{Be}_3\text{Al}_2\text{O}_6:\text{Ti}^{3+}$ .

This time we are conducting common work with Institute of Laser Physics of Russian Academy of Science for creation of laser compounds on the basis of Alexandrite and  $\text{BeAl}_6\text{O}_{10}:\text{Cr}^{3+}$ .

We firstly obtained  $\text{Be}_3\text{Al}_2\text{O}_6$  crystals  $\text{Cr}^{3+}$  doped in 1998 (Matrosov V.N. et al., 1998). Their absorption and luminescence spectra are brought on Fig. 4 and 5. It is seen that this compound will be interesting for tunable lasers. At the same time works for studying of its spectroscopy and oscillation characteristics are held.

All mentioned above compounds except  $\text{Cr}^{3+}$  and  $\text{Ti}^{3+}$  were doped by  $\text{Co}^{2+}$ ,  $\text{Ni}$ ,  $\text{Fe}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{V}^{4+}$ ,  $\text{Mn}^{3+}$ . Some of their properties are brought in the Table.

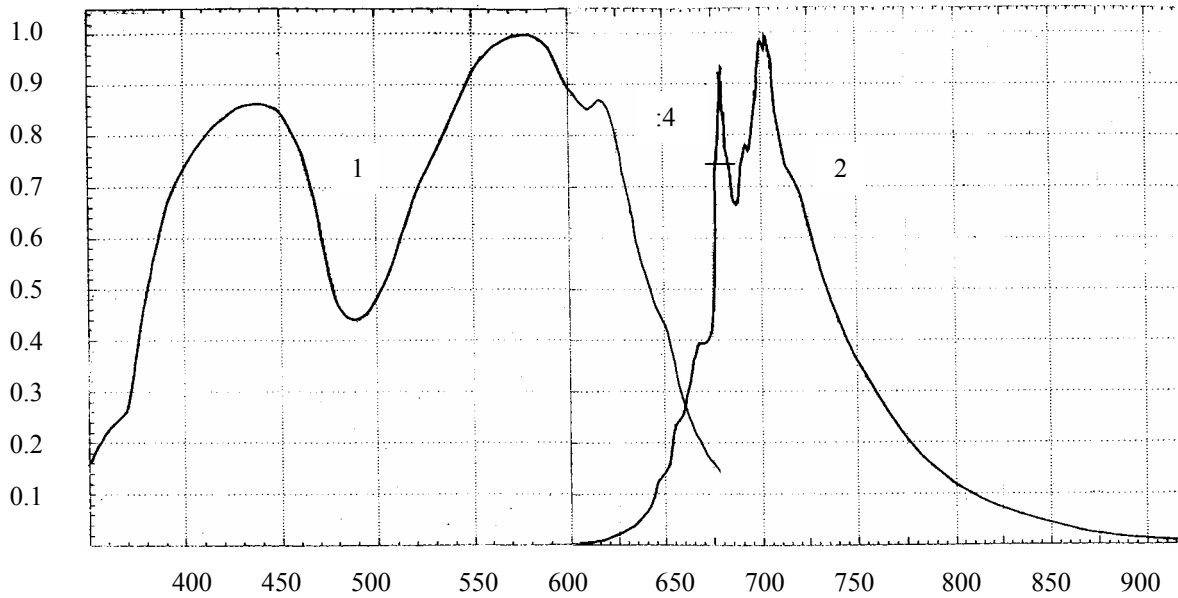
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Fig 5. Absorption (1) and luminescence spectra (2) of  $\text{Be}_3\text{Al}_2\text{O}_6:\text{Cr}^{3+}$ .

Table. Spectroscopy data d-ions in crystals.

Crystal	Luminescence range on the level 1/2, nm	Effective cross-section of transition, $10^{-19}$ , $\text{cm}^2$	Life-time, $\mu\text{sec}$
Titanium ( $\text{Ti}^{3+}$ )			
$\text{Al}_2\text{O}_3$	660 - 850	3,1	3,5
$\text{BeAl}_2\text{O}_4$	670 - 900	1,0	5,0
$\text{BeAl}_6\text{O}_{10}$	690 - 1000	3,5	1,2
$\text{Be}_3\text{Al}_2\text{O}_6$	675 - 850	-	4,0
Chromium 76 ( $\text{Cr}^{3+}$ )			
$\text{BeAl}_2\text{O}_4$	660 – 750	0,2	250
$\text{BeAl}_6\text{O}_{10}$	700 – 920	0,6	13,5
$\text{Be}_3\text{Al}_2\text{O}_6$	650-750	-	283
Vanadium ( $\text{V}^{4+}$ )			
$\text{BeAl}_2\text{O}_4$	600 – 830	1,4	2,1
Nickel ( $\text{Ni}^{2+}$ )			
$\text{BeAl}_2\text{O}_4$	1230 – 1430	0,03	600,0
$\text{BeAl}_6\text{O}_{10}$	1300 – 1550	0,02	-

### Conclusions.

1. Crystals, formed in  $\text{BeO} - \text{Al}_2\text{O}_3$ -system, were grown.
2. Courses of defects' formation in crystals were studied, and ways of their removing were found.
3. Prospects of these compounds' using in solid state lasers was shown.

The authors says thanks to Mr. Knuykshto V.N. for cooperation in field of investigation of spectrum of beryllium aluminate compounds  $\text{Cr}^{3+}$ ,  $\text{Ti}^{3+}$  - doped.

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