

$ZnSe:Cr^{2+}$ laser crystals grown by Bridgman method

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The melt growing of ZnSe crystals doped with Cr^{2+} for tunable mid-IR (2–3 μm) lasers has been described. A good quality crystal material with high homogeneity of both composition and physical properties has been obtained. The optimum concentration of dopant has been estimated. For an active element of 3 mm in thickness, it amounts to $2.3 \cdot 10^{18}$ cm^{-3}. The laser emitters have been manufactured operating with efficiency up to 70 % in continuous and pulse modes.

Описан процесс расплавного выращивания кристаллов ZnSe, легированных примесью Cr^{2+}, для перестраиваемых лазеров среднего ИК диапазона (2...3 мкм). Получен качественный кристаллический материал с высокой степенью однородности состава и физических свойств. Проведена оценка оптимальной концентрации активаторной примеси в кристаллах ZnSe, которая для активного лазерного элемента толщиной 3 мм составила $2.3 \cdot 10^{18}$ $см^{-3}$. Изготовлены лазерные излучатели, работающие с КПД до 70 % в непрерывном и импульсном режимах.

The short-wave edge of the mid-IR (2–3 μm) range of the solar radiation spectrum near the Earth surface is notable for characteristic lines of many atmospheric gases and vapors (H_2O, CO_2, CO, N_2O, HCN, etc.). The maximum optical absorption of biological tissues also falls within this range due to the predominant influence of hydroxy and amino groups. The obvious practical importance of mid-IR inspires the search for an optimal laser emitter for this range.

Lasers comprising Co^{2+} ion-doped MgF_2 crystals and emitting in the range from 1.8 to 2.4 μm are widely represented on the market among commercial emitters. These lasers, however, have relatively low efficiency due to a low luminescence yield of Co^{2+} ions in the magnesium fluoride matrix. Meantime, practical and compact semiconductor lasers based on lead salts (PbSe), antimonides (GaSb), heterojunctions and quantum cascades exhibit the output powers of several milliwatts and require cryogenic cooling to suppress the nonradiative recombination mechanisms. Lasers with rare-earth ions ($YAG:Er^{3+}$, Tm^{3+}, Ho^{3+}) have limited tuning capability in this range. Nonlinear optical converters (Raman frequency converters, optical parametric amplifiers) are complex in operation and large in size [1].

Today, the most promising material for the mid-IR range emitters is ZnSe crystal doped with Cr^{2+} ions [2, 3]. This material is chemically and mechanically stable and has high thermal conductivity. The state of chromium ions in the crystal matrix ensures that this laser medium provides the highest gain among vibronic lasers, and efficient tunability. In addition, the intrinsic lasing band from 2.1 to 3.0 μm falls within the transparency range of the matrix (Fig. 1) [4].

With $ZnSe:Cr^{2+}$ crystals as the laser medium, it has been the first successful attempt to build a laser tunable in this range operating in continuous-wave (CW) mode at room temperature [5–7]. The high efficiency and tunability of this medium allows making a universal laser for environmental monitoring (detection of noxious gas pollutants in small concentrations), optical communication in space, medicine (laser surgery and optical tomography), military applications, etc. The possibility of high-sensitivity laser spectroscopy of atmospheric air in the wavelength band from 2.41 to 2.46 μm utilizing a $ZnSe:Cr^{2+}$ laser has been demonstrated [8].

In this work, we describe the process of crystal growth from melt of Cr^{2+}-doped ZnSe. To assess the grown crystals quality and suitability for production of laser elements, their chemistry, together with mechanical, optical and dielectric parameters, was investigated. Based on the data obtained, the optimum concentration of the dopant in ZnSe crystals has been estimated.

ZnSe crystals with Cr dopant were grown by Bridgman method from melt under pressure of argon up to 15 atm in a original multi-zone growth furnace. Automatic regulation of the thermal field together with programmable modes for crystal growing and cooling provided perfect crystalline ingots of 40 mm in diameter and 80 to 100 mm in length. As containers for loading the charge material, graphite crucibles were used with a pyrocarbon reinforcing coating. The charge material was pre-synthesized zinc selenide powder of a purity not lower than 5N. Doping of the crystals was carried out by introducing chromium oxide Cr_2O_3 or pure Cr metal into the charge, followed by melt homogenization. Introduction of the chromium dopant into the charge during its melting and the melt homogenization prior to crystallization revealed an undoubted advantage of this technology over other methods of obtaining heavily doped crystals, first of all, over vapor-phase methods. The crystal ingots had a color from yellow to dark cherry, depending on the active impurity concentration in the range of 10^{17} to 10^{19} cm^{-3}.

The effectiveness of a laser is defined first of all by the active medium quality, in the case of $ZnSe:Cr^{2+}$, by the crystal lattice perfection, as well as by homogeneity of optical and other physical properties through-

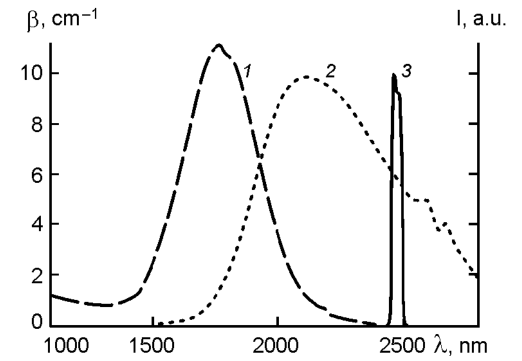

Fig. 1. Spectra of fundamental absorption (*1*), luminescence (*2*) and lasing (*3*) of $ZnSe:Cr^{2+}$ crystals.

out the active element volume and the optimum doping level.

The ZnSe:Cr system can be regarded as a substitutional solid solution of the two compounds, ZnSe–CrSe, hence, basing on the relation between their melting points, one can judge the value of the Cr segregation coefficient at the ZnSe solid-melt interface. The mentioned temperatures are very close: T_{melt}(ZnSe) = 1525°C and T_{melt}(CrSe) = 1495°C, which gives reason to assert that the segregation coefficient of Cr in ZnSe is close to unity. Our measurements of chromium concentration distribution throughout the volume of a grown crystal (Fig. 2) by chemical analysis fully confirmed this assumption. It is seen from the Figure that almost 80 % of the crystal volume is characterized by similar chromium concentrations.

The second important experimental fact is that we have shown possibility of a homogeneous doping of crystals with chromium within the whole concentration range of practical interest. This range, at which the absorption band peaked around 1.78 μm (Fig. 1) becomes distinguishable that is responsible for intracenter transitions in Cr ions [1], is limited to the minimum chromium concentration of about 10^{17} cm^{-3}.

The Cr^{2+} dopant concentration in the grown crystals was determined by inductively coupled plasma atomic emission spectrometry (ICP/AES). This method allows detection of low concentrations of metals, having a sensitivity of 10^{-3} to 10^{-5} wt. %. The research was conducted by means of a Trace Scan Advantage unit made by Thermo Jarrell Ash Corp. According to ICP/AES, the chromium concentration in $ZnSe:Cr^{2+}$ crystals falls within the range of $6.2 \cdot 10^{-4}$ to

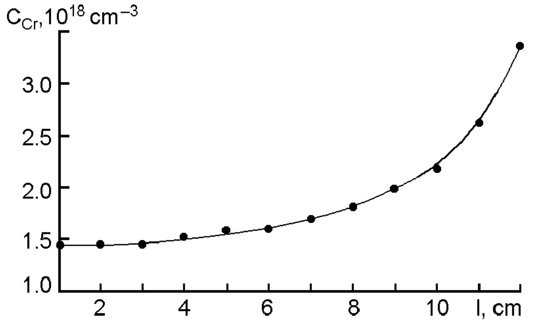

Fig. 2. Chromium concentration distribution along the crystal growth axis.

$4.9 \cdot 10^{-3}$ wt. %, which corresponds to $3.8 \cdot 10^{17}$–$3 \cdot 10^{18}$ cm^{-3}.

To control the content of a wide variety of impurities (about 75 elements), the laser mass spectrometry was employed. The experimental setup consists of a high-resolution double-focusing laser mass spectrometer MS 3101, and recording microphotometer IFO-451. The random error of the analysis is characterized by the relative standard deviation of 0.15 to 0.3. The study has revealed trace impurities of several most abundant elements (e.g., metal impurities: Fe, Al, Mg, Cu, as well as oxygen and carbon). According to the research, the average concentration of the mentioned impurities did not exceed 10^{-5} wt. %. It is known that such a concentration level of technological impurities cannot significantly impact the crystal optical parameters.

The ultimate stress limit of grown crystal samples was determined by mechanical compression tests on an "Instron" type test machine at room temperature. The ultimate stress limit was defined as the stress, at which the first crack appeared. The results obtained (see Table) indicate that the ultimate stress limit along the [110] direction is somewhat higher than that along [111], and increases towards the ingot heel. The hardening is likely related to the rejection and accumulation of impurities towards the crystal heel. For all the crystallographic directions considered, the ultimate stress limit of $ZnSe:Cr^{2+}$ crystals falls within the range from 4 to 11 kg/mm^2, which meets the requirements for power laser optical elements.

Mechanical properties of $ZnSe:Cr^{2+}$ crystals were also studied using concentrated loading. The microhardness was measured on a cleavage plane by the standard technique on the PMT-3 setup under 100 g load. The results showed the value of microhardness of 111 kg/mm^2, i.e. it does not differ

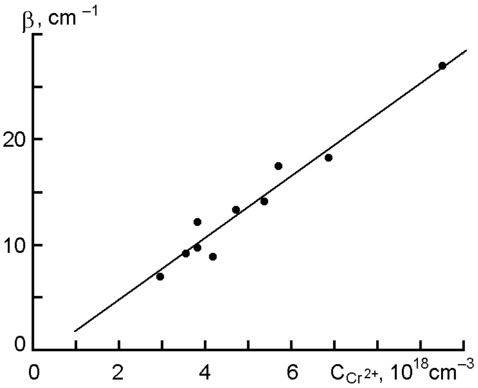

Fig. 3. Dependence of the linear light absorption coefficient at 1.78 μm wavelength on the chromium concentration in a $ZnSe:Cr^{2+}$ sample.

from the one typical for undoped zinc selenide crystals. No anisotropy of microhardness of first kind on the cleavage plane is observed; the anisotropy factor being $k = 1$.

The examination of $ZnSe:Cr^{2+}$ crystal cleavages in polarized light passing through crossed Nicol prisms has shown no birefringence bands. This fact indicates that doping with chromium leads to disappearance of twin bands, which are characteristic for undoped ZnSe crystals grown from melt by Bridgman method. The absence of twin bands and of first kind microhardness anisotropy shows that the doping zinc selenide crystals with chromium in the studied concentrations range results in a stabilization of the crystal structure.

The real and imaginary parts of complex permittivity $\varepsilon^* = \varepsilon' + \varepsilon''$ have been measured as functions of the measuring field frequency ($f = 5 \cdot 10^2$–$2 \cdot 10^8$ Hz) and temperature (T = 300–500 K) using the scanning dielectric spectroscopy [9, 10]. It was found that variation of Cr^{2+} dopant concentration in the range of 10^{17}–10^{19} cm^{-3} is accompanied by variation of ε'' by two to three orders of magnitude without appreciable change of ε'. The doping also causes an important increase in both parameters with temperature. The dependences $\varepsilon'(T)$ and $\varepsilon''(T)$ are activational in nature. Their appearance is changed when an uniaxial compression is applied to the sample (σ = 2 kgf/cm^2).

Basing on the experimental data obtained, the optimum dopant concentration in the grown $ZnSe:Cr^{2+}$ crystals has been estimated. The main criterion was the complete and homogeneous absorption of pumping radiation in the laser crystal combined with a high lasing efficiency.

The upper acceptable limit of the chromium ion concentration in ZnSe crystals is defined by the dependence of the photoluminescence lifetime σ_{PL} on the crystal doping level. As is known from [11], introduction of chromium at concentrations exceeding $3 \cdot 10^{19}$ cm^{-3} leads to a sharp drop in the σ_{PL} value and, therefore, reduction in the $ZnSe:Cr^{2+}$ lasing efficiency.

The dependence of the absorption factor at the pumping wavelength (1.78 μm) $\beta_{1.78}$ on the activator concentration in the grown crystals was measured. It is seen from Fig. 3 that the $\beta_{1.78}$ value varies from 1.5 to 28 cm^{-1} and may be sufficient for a significant inhomogeneity of the pumping radiation absorption in laser elements. The distribution homogeneity of the energy absorbed in a hypothetical crystal sample shaped as a parallelepiped of 3 mm thickness typical of a laser active element, was considered involving the Bouguer-Lambert-Beer law:

$$I_x = I_0 \exp^{-\beta_{1.78} x}, \quad (1)$$

where I_0 is the radiation intensity at the input plane; I_x, that at a distance x from the input plane.

Fig. 4 shows the theoretical dependence of the optical transmittance I_x/I_0 on the crystal sample thickness x. To plot a set of curves, the absorption coefficients closest to the actual ones at the pumping radiation wavelength of 1.78 μm were used. It can be concluded from the Figure that at $\beta_{1.78}$ = 3 cm^{-1} only about half the pumping energy will be absorbed in the crystal, and at $\beta_{1.78}$ = 8 cm^{-1}, over 90 % of the pumping energy will be absorbed, but its distribution over the sample thickness will be highly inhomogeneous. In practice, such a distribution may cause overheating of a thin layer of the semiconductor, which would significantly reduce the lasing efficiency. It follows that the optimum absorption coefficient for pumping radiation may be as high as $\beta_{1.78}$ = 5 cm^{-1},

Table. Ultimate stress limit of $ZnSe:Cr^{2+}$ crystals along different crystallographic directions

Ingot part	Ultimate stress limit, kg/mm^2	
	Compression direction [111]	Compression direction [110]
nose	3.9	6.9
center	3.7	4.4
heel	6.1	10.9

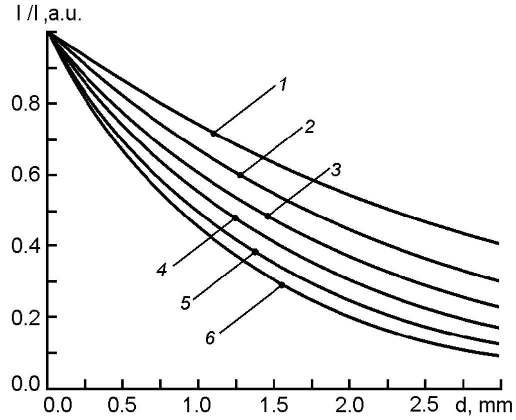

Fig. 4. Dependences of optical transmittance on the crystalline sample thickness. Parameters of optical absorption b is equal to 3 cm^{-1} (*1*), 4 cm^{-1} (*2*), 5 cm^{-1} (*3*), 6 cm^{-1} (*4*), 7 cm^{-1} (*5*), 8 cm^{-1} (*6*).

the corresponding optimal concentration of chromium in the crystal being $2.3 \cdot 10^{18}$ cm^{-3}.

Two optical layouts of laser emitters making use of our $ZnSe:Cr^{2+}$ crystals were designed and tested at General Physics Institute of Russian Academy of Sciences (Moscow) and Czech Technical University (Prague) [12, 13]. The first layout implied pumping by a laser on erbium ions (Er^{3+}) in the yttrium-aluminum perovskite ($YAlO_3$) matrix at 1.66 μm wavelength. The emitter operated in a pulse mode with the efficiency of 70 %. The pulses have been obtained of 120 μs duration and the repetition rate of 1 GHz. The pulse energy is 14 mJ. The second layout utilized pumping by a laser on thulium ions (Tm^{3+}) in $YAlO_3$ matrix at 1.97 μm wavelength. The emitter operated in the CW mode with the 66 % efficiency. The output power reached its maximum at 195 mW. The spatial structure of a radiation beam with thulium laser pumping is close to the Gaussian shape that corresponds to the principal mode. This indicates a high homogeneity degree of the laser crystal.

Thus, the results of this work indicate a significant potential of the $ZnSe:Cr^{2+}$ laser crystal melt-growth technology developed at Institute for Single Crystals, NAS of Ukraine. A high-quality crystal material with a high homogeneity of the composition and physical properties has been obtained. The optimum dopant concentration in ZnSe crystals has been estimated. Laser emitters have been prepared operating with efficiency of up to 70% in both the CW and pulsed modes.

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Лазерні кристали ZnSe:Cr^{2+}, що вирощені методом Бриджмена

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Описано процес розплавного вирощування кристалів ZnSe, легованих домішкою Cr^{2+}, для перестроюваних лазерів середнього ІЧ діапазону (2...3 мкм). Отримано якісний кристалічний матеріал з високим ступенем однорідності складу та фізичних властивостей. Проведено оцінку оптимальної концентрації активаторної домішки у кристалах ZnSe, яка для активного лазерного елемента товщиною 3 мм склала $2{,}3\cdot10^{18}$ см$^{-3}$. Виготовлено лазерні випромінювачі, що працюють із ККД до 70 % у безперервному й імпульсному режимах.