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Dependence of $PbMoO_4$ crystal damage threshold on Nd^{3+} concentration and method of doping

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$PbMoO_4:Nd^{3+}$ crystals with the activator concentration up to 3 wt.% were grown by the Czochralski method. The damage threshold and incorporation coefficient dependences on the activator concentration and the method of doping were determined. The internal stress concentrations in $PbMoO_4:Nd^{3+}$ crystals were estimated by means of optical polarization method.

Кристаллы $PbMoO_4:Nd^{3+}$ с концентрацией активатора до 3 мас.% выращены методом Чохральского. Определены коэффициент вхождения и лучевая прочность в зависимости от концентрации активатора и метода его введения. Уровень внутренних напряжений в кристаллах $PbMoO_4:Nd^{3+}$ оценен при помощи оптического поляризационного метода.

1. Introduction

To expand the laser generation band, the effect of stimulated Raman scattering (SRS) in solids can be successfully applied [1]. The use of active laser media combining the laser generation function and SRS-conversion makes it possible to simplify the laser design and raise the laser system efficiency. It is known that lead tungstate $PbWO_4$ (PWO) and lead molybdate $PbMoO_4$ (PMO) single crystals with scheelite-type structure (sp.gr. $I4_1/a$) possess the maximum SRS integral intensities among the crystals with different quasi-molecular anions [1, 2]. This fact should provide high SRS conversion efficiency and ~900 cm^{-1} shift of the laser wavelength caused by interaction of laser active ion generation with the vibration modes of $(WO_4)^{2-}$ or $(MoO_4)^{2-}$ anions.

In [3] laser and self-Raman laser generations in $PMO:Nd^{3+}$ crystal were obtained under 1.5 W laser diode (LD) pumping. Thereat, the self-Raman output pulse energy was equal to 6 μJ (1^{st} Stokes component, $\lambda = 1163$ nm) at 500 ps pulse duration. To generate the Stokes components effectively, much higher pumping power should be applied. Therefore, in the present study we investigated the radiation damage threshold of $PMO:Nd^{3+}$ crystals depending on the concentration of Nd^{3+} and the doping method.

2. Experimental

Pure and Nd^{3+}-doped PMO single crystals were grown in air from 100 cm^3 and 500 cm^3 Pt-crucibles by the Czochralski method using the "Analog" automatic setup equipped with a weight control system. The crystals were grown onto a seed oriented along the direction [001]. This direction was chosen due to a cylindrical morphology of crystal and a simple production procedure of oriented sample. The growth

Table 1. Time-temperature conditions of solid state synthesis

Sample	Temperature, °C	Duration, h	Phase content, wt.%
$PbMoO_4$	650	10	97±2
$NaNd(MoO_4)_2$	650	10	96±2
$Nd_2(MoO_4)_3$	800	10	95±2
$NdNbO_4$	1100	10	96±2

parameters for all the crystals were: the temperature gradient $T_z = 50–70$ deg/cm, the rotation rate $\omega = 20–30$ min^{-1}, the pulling rate $V_z = 1–3$ mm/h. The variation of growth parameters in these ranges allowed us to grow PMO crystals up to 40 mm and a length up to 150 mm. The PMO crystals chosen for investigation were of up to 25 mm in diameter and up to 50 mm long. All PMO crystals to be investigated were grown under the same conditions (at fixed values of temperature gradient, rotation and pulling rates). In our experiments the value H/D (ratio of height of crystal cone to diameter of crystal) was ~0.25. All the crystals were free of impurity phases and macroscale defects (gas bubbles, crystal cracking). The pure crystals had a yellowish color, Nd^{3+} doped crystals were lilac. The color intensity of doped PMO crystals depended on Nd^{3+} concentration.

To dope PMO crystals, we used Nd_2O_3, as well as presynthesized $Nd_2(MoO_4)_3$, $NaNd(MoO_4)_2$ and $NdNbO_4$ compounds. When Nd_2O_3 and $NdNbO_4$ compounds were used, the ratio PbO/MoO_3 in the PMO melt was stoichiometric, while with $Nd_2(MoO_4)_3$ and $NaNd(MoO_4)_2$ the PMO melt was enriched with MoO_3. The starting chemical reagents were: PbO, Nb_2O_5, Na_2CO_3 and Nd_2O_3 — 99.99 %, MoO_3 — 99.95 %. The synthesis of PMO and dopants was carried out according to the ceramic technology. The stoichiometric blend of starting reagents was heated to the defined temperature and kept for the defined time. The temperature-time regimes of the solid state synthesis are presented in Table 1. The X-ray structure studies were carried out on a SIEMENS D500 automated diffractometer in CuK_α radiation ($\lambda = 1.5418$ Å, graphite monochromator) using the $2\theta/\theta$ scanning method at rates 0.24 grad/min. The incorporation coefficient K_{Nd} was calculated as ratio of Nd concentration in crystal to Nd concentration in melt.

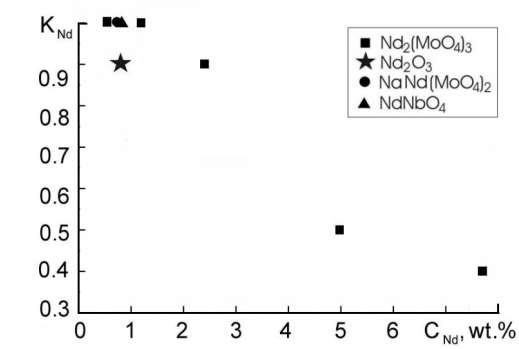

Fig. 1. Dependences of the K_{Nd} on Nd concentration in the $PbMoO_4$ melt.

The content of Nd^{3+} in PMO crystals was determined by means of inductively coupled plasma analysis (PRACE SCAN Advantage spectrometer). To determine Nd^{3+} concentration in PMO:Nd^{3+} crystals, a specimen was cut off from central part of every ingot. The damage threshold and internal stresses were studied on oriented polished $10\times10\times10$ mm^3 crystal samples produced from the central cylindrical part of each crystal. Under He–Ne laser beam passing through a sample no scattering was observed. In the first instance the axial angle had been measured, hereafter the same samples were used for the damage threshold definition.

To determine the damage threshold, YAG:Nd^{3+} pulsed laser ($\lambda = 1.06$ μm, TEM_{00}-mode, 10 ns pulse duration, 1 Hz repetition rate, the spot diameter ~45 μm, Gaussian distribution of intensity) was used.

The axial angle 2V was measured by means of optical polarization method using a MIN-8 polarizing microscope according to the procedure described in [4]. The instrument magnification was 70.5. The said angle was determined for every sample as the average for three points located on the plane (001).

3. Results and discussion

For total absorption of LD pumping energy, heavy Nd^{3+}-doped laser active media are required. Therefore, we investigated the dependence of K_{Nd} value on the activator concentration in the PMO melt and the doping method. To grow Nd^{3+} doped PMO crystals, isostructural ($Nd_2(MoO_4)_3$, $NaNd(MoO_4)_2$) and non-isostructural (Nd_2O_3, $NdNbO_4$) compounds were used, as well as charge-compensating ions Na^+ ($NaNd(MoO_4)_2$) and Nb^{5+}

($NdNbO_4$). The K_{Nd} concentration dependence is presented in Fig. 1.

As seen from Fig. 1, K_{Nd} ~ 1 for the concentrations up to ~1 wt.%. An exception is Nd_2O_3 case, where K_{Nd} ~ 0.9. At further increase of the Nd concentration in the melt the coefficient K_{Nd} is decreased (Nd^{3+} doping by means of $Nd_2(MoO_4)_3$).

According to [5, 6], the system $PbMoO_4$–$Nd_2(MoO_4)_3$ contains the solid solutions in the whole concentration range. By comparing the ionic radii of Pb^{2+} (1.26 Å) and Nd^{3+} (0.99 Å) one can assume that the coefficient K_{Nd} will be approximately ~1. However, as seen from Fig. 1, the decrease of K_{Nd} in PMO crystals begins from ~1 wt.% in the melt, and at 7.7 wt.% the coefficient is equal to 0.4.

The coefficients K_{Na} and K_{Nb} were not determined. But according to the data of X-ray analisys the parameters of PMO:Nd^{3+} unit cell are different under the same Nd concentrations at use of $Nd_2(MoO_4)_3$, $NaNd(MoO_4)_2$ and $NdNbO_4$ compounds (Table 2). This fact allows us to conclude that Na^+ and Nb^{5+} build in PMO crystal lattice too.

Our measurements of the damage threshold show that the maximum value of optical break- down J_{Th} ~ 90 J/cm^2 is achieved at use of Nd_2O_3 (the concentration of Nd^{3+} in the crystal is 0.8 wt.%, Fig. 2). It should be noted that in the case of $Nd_2(MoO_4)_3$ introduction (the Nd^{3+} concentration in the crystal is 0.8 wt.%) the damage threshold J_{Th} ~ 60 J/cm^2 is close to that of a pure PMO crystal. Co-doping with Nb^{5+} does not affect the damage threshold value dramatically: under such conditions — J_{Th} ~ 58 J/cm^2, but the use of Na^+ practically halves the magnitude of optical break-down: in this case J_{Th} ~ 29 J/cm^2. At further growth of the Nd concentration in PMO crystal the damage threshold J_{Th} is decreased.

There are few types of physical effects leading to the optical breakdown. The first one is conditioned by the interaction of laser radiation with impurities or absorbing inclusions. The next one is connected with nonlinear effects (self-focusing, multiphoton absorption), when the space-time distortion of laser radiation is going on in a dielectric crystal. The last effect, self laser induced breakdown happens when the space-time distortion of laser radiation is not in a crystal [7]. On one hand the damage threshold will be a result of laser radiation absorption by impurities, but on other hand impurities are able to improve the optical breakdown dramatically by means of electron trap forming [8]. At further growth of impurity content in a crystal the probability of phase inclusion forming or other absorbing heterogeneity forming is increased and the damage threshold is decreased.

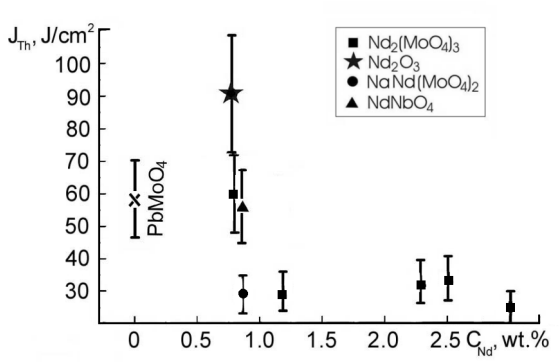

Fig. 2. Dependences of the damage threshold J_{Th} on Nd concentration in the $PbMoO_4$ crystal.

As it was shown in [9, 10] the anionic group $(WO_4)^{2-}$ is kept in melts of simple and double sheelite like tungstates. In our case we can suppose that at use of $Nd_2(MoO_4)_3$ and $NaNd(MoO_4)_2$ compounds the anionic groups $(MoO_4)^{2-}$ are kept in melt too. At the same time the use of Nd_2O_3 leads to the O^{2-} containing melt. Thus, the use of different compoumds for Nd doping can affect structure of melt and predetermine an activator center structure.

According to the hypothesis proposed in [11] on the base of dielectric response measurements of PWO:Nd^{3+} crystals, at low Nd^{3+} concentrations these ions build in the Pb^{2+}

Table 2. Parameters of the $PbMoO_4$:Nd unit cell at use of different dopants

Parameter	Compound; Nd concentration in the crystal, wt.%				
	Pure	Nd_2O_3; 0.75	$Nd_2(MoO_4)_3$; 0.8	$NaNd(MoO_4)_2$; 0.8	$NdNbO_4$; 0.8
a, Å	5.43641(8)	5.43394(3)	5.43389(4)	5.43099(4)	5.43386(4)
c, Å	12.10786(9)	12.10095(11)	12.,10049(13)	12.08866(12)	12.08813(12)
V, Å^3	357.844(4)	357.313(5)	357.293(5)	356.563(5)	356.925(5)

sublattice and form $(2Nd_{Pb}^{3+})^{\bullet} - (V_{Pb})''$ activator center, the excessive positive charge being compensated by lead vacancy. In heavily Nd^{3+} doped PWO crystals more sophisticated activator center $(Nd_W^{3+})'''-(Nd_{Pb}^{3+})^{\bullet}-(V_O)^{\bullet\bullet}$ is formed; thereat Nd^{3+} is built in the Pb^{2+} and W^{6+} sublattices, the excessive negative charge is compensated by oxygen vacancy. In all the cases the PWO crystals reported in [11] were doped with Nd_2O_3. Obviously, a structure of Nd^{3+} activator center will be determined by a crystallographic position of Nd^{3+} ion in PMO lattice and charge compensating defect and will depend on Nd concentration and method of doping.

The presence of internal stresses in the crystal which are induced by crystal growth technology and impurities may considerably affect the magnitude of optical breakdown. The absorption of laser radiation by absorbing heterogeneity leads to the heating of local region with following extension. This is caused by the fact that under irradiation of the crystal with nanosecond laser pulses, the mechanism of crystal cracking connected with accumulation of thermo-elastic stresses, is realized [12, 13].

Therefore, we estimated the level of structure perfection from the distortion of isogyres in the interference pattern observed at passage of polarized light along the direction [001]. Internal stresses give rise to anomalous biaxiality in the crystal, and the axial angle 2V is proportional to the level of these stresses. So, we measured the axial angle 2V for all the doped and co-doped PMO crystals using the optical polarization method. The obtained data are presented in Fig. 3.

The pure and Nd^{3+} containing PMO crystals (<1 wt. %) where isostructural compounds ($Nd_2(MoO_4)_3$, $NaNd(MoO_4)_2$) were used, are characterized by the minimum magnitudes of 2V angle varying between 27′ and 32′. The introduction of the non-isostructural compounds (Nd_2O_3, $NdNbO_4$) in the PMO melt raises the value of 2V angle up to 43′–47′. At further increase of Nd^{3+} concentration in the PMO crystal internal stresses grow. The heavily doped PMO crystal (3 wt.%) showed the maximum magnitude of 2V angle — 1°2′.

Note that the PMO:Nd^{3+} crystals with the highest level of internal stresses at <1 wt.% concentrations of the activator possess the maximum magnitudes of damage threshold, too. Therefore, the most probable factor which causes optical breakdown in PMO:Nd^{3+} crystals at these concentrations may be the compensating excessive charge defect.

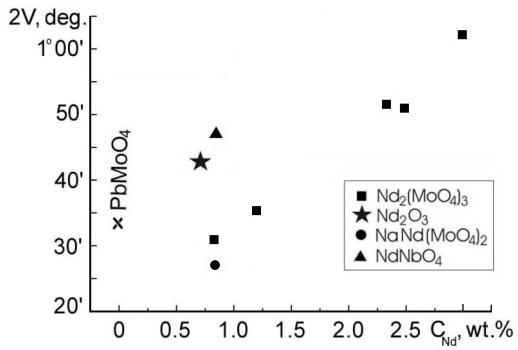

Fig. 3. Dependences of the axial angle 2V on Nd concentration in the $PbMoO_4$ crystal.

4. Conclusion

$PbMoO_4$:Nd^{3+} crystals with the activator concentration up to 3 wt.% were grown by the Czochralski method. Few doping methods (Nd introduction in the form of isostructural and non-isostructural compounds, co-activation) were used. It was shown, that incorporation coefficient K_{Nd} equals to ~1 for the concentrations up to ~1 wt.% at the use of $Nd_2(MoO_4)_3$, $NaNd(MoO_4)_2$ and $NdNbO_4$ dopants. An exception is Nd_2O_3 case, where $K_{Nd} \sim 0.9$. At further increase of the Nd concentration in the melt at $Nd_2(MoO_4)_3$ doping the coefficient K_{Nd} is decreased.

The damage threshold was studied depending on the activator concentration and the method of doping too. It was established that the maximum magnitude of damage threshold 90 J/cm^2 was achieved at 0.75 wt.% Nd concentration in the PMO crystal. Thus from practical view point the use of Nd_2O_3 for PMO doping is more effectual because of simpler procedure of PMO:Nd^{3+} crystal production (there is no necessity of compound synthesis for doping) and high magnitude of the damage threshold. The level of structure perfection of PMO:Nd^{3+} crystals was estimated by means of axial angle 2V measurements.

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Залежність променевої стійкості кристалів $PbMoO_4$ від концентрації Nd^{3+} та способу активування

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Кристали з концентрацією активатора до 3 мас.% вирощено методом Чохральського. Визначено коєфіцієнт входження та променеву стійкість в залежності від концентрації активатора та метода його введення. Рівень внутрішніх напруженнь у кристалах $PbMoO_4$:Nd^{3+} оцінено за допомогою оптичного полярізаційного методу.