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OPTICAL STUDY OF SrLaGaO_4 AND $\text{SrLaGa}_3\text{O}_7$ DOPED WITH Nd^{3+} AND Yb^{3+}

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Single crystals of SrLaGaO_4 and $\text{SrLaGa}_3\text{O}_7$ singly doped with Nd and codoped with Nd and Yb have been grown by the Czochralski method. Both the compounds form tetragonal crystals but belong to different space groups. A common feature of these matrices is a structural disorder resulting from statistical distribution of Sr^{2+} and La^{3+} ions over the lattice sites. A previous investigation of a laser diode pumped $\text{SrLaGa}_3\text{O}_7:\text{Nd}$ laser revealed that inhomogeneous broadening of spectral lines of Nd^{3+} was advantageous for optical pumping and did not influence adversely the extraction efficiency. The present paper deals mainly with optical properties of Yb^{3+} ions which are of interest for the design of lasers pumped by a diode laser and operating near $1 \mu\text{m}$.

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1. Introduction

Interest in $\text{SrLaGa}_3\text{O}_7$ and SrLaGaO_4 crystals doped with Nd and Yb is related to their application as active media for the design of all-solid state lasers. A common feature of both the crystals is a structural disorder associated with a random distribution of Sr^{2+} and La^{3+} ions. The distorted structure induces an important inhomogeneous broadening of spectral bands in activated crystals, thereby influencing their laser performance. A broad absorption band matches better the emission band of a diode laser thus improving the absorption efficiency. On the other hand, an inhomogeneous broadening of emission band may reduce the extraction efficiency. The latter effect should be small when a high laser efficiency is needed. It appears that this condition is fulfilled in the case of a laser diode pumped $\text{SrLaGa}_3\text{O}_7:\text{Nd}$ laser, which showed an optical slope efficiency of about 50% [1]. Considerably lower efficiencies were recorded during investigation of $\text{SrLaAlO}_4:\text{Nd}$ laser crystal [2]. Poor laser performance of this material has been attributed to reduced extraction efficiency due to very large emission band width. In this paper we

report on spectroscopic properties relevant to potential laser emission near $1\ \mu\text{m}$, associated with the ${}^2F_{5/2}$ - ${}^2F_{7/2}$ transition of Yb^{3+} in $\text{SrLaGa}_3\text{O}_7$ and SrLaGaO_4 crystals.

The single excited level ${}^2F_{5/2}$ of Yb may be populated directly using an InGaAs laser diode operating near $1\ \mu\text{m}$. An alternative way of optical pumping of ytterbium laser consists of an excitation of Nd^{3+} in Nd-Yb codoped crystal using an AlGaAs laser diode operating near $0.8\ \mu\text{m}$ and of subsequent nonradiative Nd-Yb energy transfer. Appropriate optical pumping may be chosen taking into account spectral properties of a material. However, the main shortcoming of solid-state lasers based on Yb ion involves the quasi-four-level scheme. Therefore, a large crystal field splitting of the ground ${}^2F_{7/2}$ multiplet and strong transitions to higher lying crystal field components are of paramount importance for the design of low threshold ytterbium lasers.

2. Crystal structure

$\text{SrLaGa}_3\text{O}_7$ belongs to the large family of compounds of general chemical formula ABC_3O_7 , where A = Ca, Sr, Ba; B = Y, La-Gd; C = Al, Ga. ABC_3O_7 compounds form tetragonal crystals belonging to the space group $P42_1m$. The crystal structure is built up from CO_4 layers formed in the ab plane. Between the layers the divalent A cations and trivalent B cations are distributed randomly in eight coordinated sites with C_2 symmetry. SrLaGaO_4 belongs to the large family of compounds of general chemical formula ABCO_4 , where A = Ca, Sr; B = Y or rare earth element; C = Al, Ga or transition metal. ABCO_4 compounds form tetragonal crystals with the K_2NiF_4 type of structure $I4/mmm$. The crystals are built up from CO_6 layers formed in the ab plane. Between the layers the divalent A cations and trivalent B cations are distributed randomly in nine coordinated sites with C_{4v} symmetry.

3. Experimental

Single crystals of $\text{SrLaGaO}_4:\text{Nd}$, $\text{SrLaGaO}_4:\text{Nd}:\text{Yb}$ and $\text{SrLaGa}_3\text{O}_7:\text{Nd}:\text{Yb}$ have been grown by the Czochralski method. Three samples were used in this study. SrLaGaO_4 single doped with neodymium contained 0.6 at.% of Nd^{3+} , codoped sample contained 0.8 at.% of Nd^{3+} and 0.45 at.% of Yb^{3+} . $\text{SrLaGa}_3\text{O}_7$ crystal contained 0.75 at.% of Nd^{3+} and 0.3 at.% of Yb^{3+} . Absorption spectra were measured with a Varian model 2300 absorption spectrophotometer. Luminescence spectra were excited by a 514 nm line of an argon ion laser. The spectra were analyzed with a Zeiss model GDM 1000 grating monochromator, detected by a cooled photomultiplier and resulting signal was averaged by a SRS 250 boxcar integrator. In luminescence decay measurements a nitrogen laser pumped tunable dye laser was used as an excitation source. For low temperature measurements the samples were placed in an Oxford model CF 1204 continuous flow helium cryostat equipped with a temperature controller.

4. Results and discussion

4.1. Spectroscopic properties of Nd^{3+} in SrLaGaO_4

Optical properties of $\text{SrLaGa}_3\text{O}_7:\text{Nd}$ are well documented [3, 4] and the published data are used as a reference in this work. However, we are not aware of previous investigation of Nd^{3+} in SrLaGaO_4 . Therefore, a SrLaGaO_4 crystal singly doped with Nd was prepared and examined. A room temperature polarized absorption spectrum of $\text{SrLaGaO}_4:\text{Nd}$ is shown in Fig. 1. It can be seen that in

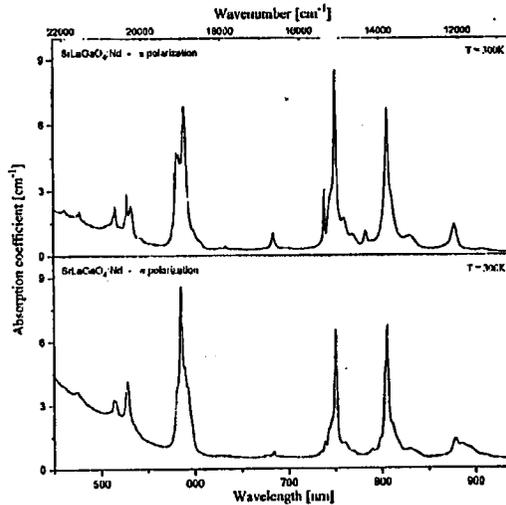


Fig. 1. Polarized absorption spectra of $\text{SrLaGaO}_4:\text{Nd}$ crystal recorded at room temperature. The thickness of the sample was 6.95 cm and the Nd^{3+} concentration was 0.8 at. %.

addition to Nd^{3+} absorption lines, a broad absorption appears at wavelengths shorter than about 500 nm. The origin of this absorption is not clear, it may be associated with structural defects created during the crystal growth. Mean oscillator strengths for Nd^{3+} lines have been evaluated from unpolarized spectrum which was recorded using a composite sample consisting of one plate which was perpendicular to the optical axis and a second one which was parallel to the optical axis of the crystal. The obtained experimental results and those calculated within the framework of the Judd-Ofelt theory are given in Table I. Three Ω parameters $\Omega_2 = 0.526 \times 10^{-19} \text{ cm}^2$, $\Omega_4 = 0.479 \times 10^{-19} \text{ cm}^2$ and $\Omega_6 = 0.753 \times 10^{-19} \text{ cm}^2$ were next used to calculate radiative transition rates and branching ratios for the ${}^4F_{3/2}$ emission. These data are included in Table II. Calculated radiative lifetime of the ${}^4F_{3/2}$ level amounts to 125 μs , whereas the luminescence lifetime recorded at low Nd^{3+} concentration is higher by about 20%. Basing on good agreement between experimental and calculated oscillator strengths we attribute this discrepancy to uncertainty of Nd^{3+} concentration.

TABLE I

Measured and calculated oscillator strengths for Nd^{3+} in SrLaGaO_4 at 300 K. All transitions are from the ${}^4I_{9/2}$ level to the level indicated.

Level	Average wavelength [nm]	Oscillator strength $P \times 10^8$		Residuals $\Delta P \times 10^8$
		meas.	calc.	
${}^4F_{3/2}$	850–920	317	357	–40
${}^4F_{5/2}, {}^2H_{9/2}$	777–847	1370	1320	+50
${}^4F_{7/2}, {}^4S_{3/2}$	725–775	1420	1457	–37
${}^4F_{9/2}$	670–710	87	108	–21
${}^2H_{11/2}$	620–650	29	30	–1
${}^4G_{5/2}, {}^2G_{7/2}$	565–615	2980	2980	0

TABLE II

Calculated radiative transition rates A , resulting radiative lifetimes τ and luminescence branching ratios β for the ${}^4F_{3/2}$ level of Nd^{3+} in $\text{Nd}:\text{SrLaGaO}_4$ crystal.

$[L', S']J'$	λ [nm]	A [s^{-1}]	τ [μs]	β
${}^4I_{15/2}$	1800	48	20833	0.006
${}^4I_{13/2}$	1330	893	1120	0.111
${}^4I_{11/2}$	1060	4203	238	0.526
${}^4I_{9/2}$	890	2857	350	0.357

4.2. $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer and optical properties of Yb^{3+}

Overlapping of Nd^{3+} emission and Yb^{3+} absorption in the two matrices is shown in Fig. 2 and the energies of excited states involved in nonradiative energy transfer are given in Table III. It can be seen that the process of energy transfer has to be assisted by phonons. An energy mismatch between Nd^{3+} emission and Yb^{3+} absorption cannot be determined precisely from optical spectra because a broad and unresolved absorption band of Yb^{3+} prevents the location of all the crystal field levels of the ${}^2F_{5/2}$ multiplet. Nevertheless, one can note that this energy mismatch is higher than the cut-off frequency of lattice vibrations which is about 750 cm^{-1} in both the matrices. In Fig. 3 we present the 5 K and 300 K emission spectra excited by a 514 nm line of an argon ion laser. In both the matrices two intense bands centered at about 9300 cm^{-1} and 11300 cm^{-1} correspond to the ${}^4F_{3/2} - {}^4I_{11/2}$ and ${}^4F_{3/2} - {}^4I_{9/2}$ transitions of Nd^{3+} , respectively. The Yb^{3+} emission, at about 10200 cm^{-1} , is considerably more intense in SrLaGaO_4 , partly because of higher Yb^{3+} concentration in this matrix. At room temperature the Nd–Yb energy transfer in $\text{SrLaGa}_3\text{O}_7$ is very weak but it becomes more important when the sample temperature decreases. The Nd^{3+} lifetime in Nd–Yb codoped $\text{SrLaGa}_3\text{O}_7$ is

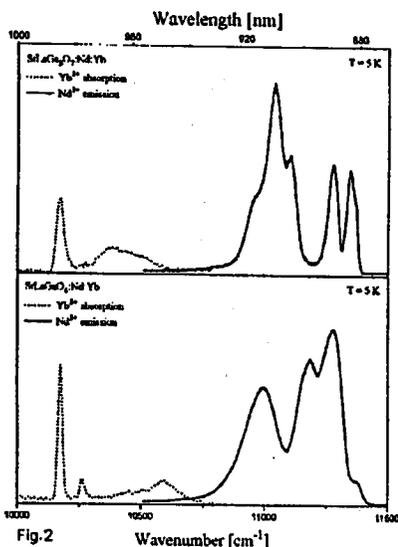


Fig.2

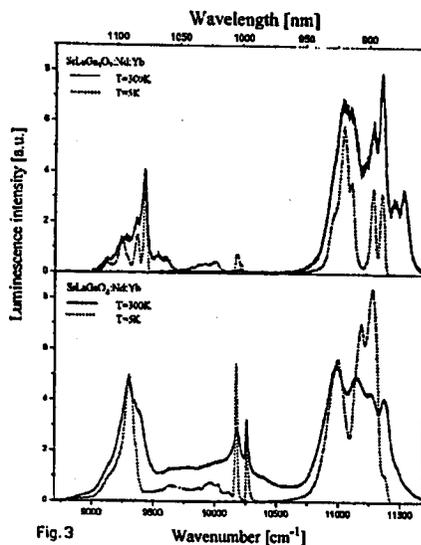


Fig.3

Fig. 2. Overlapping of Nd^{3+} emission and Yb^{3+} absorption at 5 K in $\text{SrLaGa}_3\text{O}_7$ and SrLaGaO_4 codoped with Nd^{3+} and Yb^{3+} .

Fig. 3. 5 K and 300 K luminescence spectra of $\text{SrLaGa}_3\text{O}_7$ and SrLaGaO_4 crystals codoped with Nd and Yb. Luminescence was excited by a 514 nm line of an argon ion laser. Bands centered at about 9200 cm^{-1} and at 11200 cm^{-1} are associated with the ${}^4F_{3/2}-{}^4I_{11/2}$ and ${}^4F_{3/2}-{}^4I_{9/2}$ transitions of Nd^{3+} . A band centered at about 10200 cm^{-1} corresponds to the ${}^2F_{5/2}-{}^2F_{7/2}$ transition of Yb^{3+} .

TABLE III

Mean energies of the crystal field levels split out of the ${}^4F_{3/2}$ multiplet of Nd^{3+} and ${}^2F_{5/2}$ multiplet of Yb^{3+} in $\text{SrLaGa}_3\text{O}_7$ and SrLaGaO_4 at 5 K.

Energy levels [cm^{-1}]			
$\text{SrLaGa}_3\text{O}_7$		SrLaGaO_4	
Nd^{3+}	Yb^{3+}	Nd^{3+}	Yb^{3+}
11350	10170	11380	10174
11530	10210	11514	10261
	10383		10272

found to be $285\ \mu\text{s}$ at 300 K but only $220\ \mu\text{s}$ at 5 K. In SrLaGaO_4 the Nd^{3+} lifetime of $160\ \mu\text{s}$ drops to $130\ \mu\text{s}$ in the presence of Yb^{3+} . In contrast to $\text{SrLaGa}_3\text{O}_7$, the Nd–Yb energy transfer in this matrix depends weakly on temperature in the 5–300 K region.

In Fig. 4 the 5 K absorption and emission spectra of Yb^{3+} in the two matrices are compared. These spectra indicate that Yb^{3+} ions are distributed in

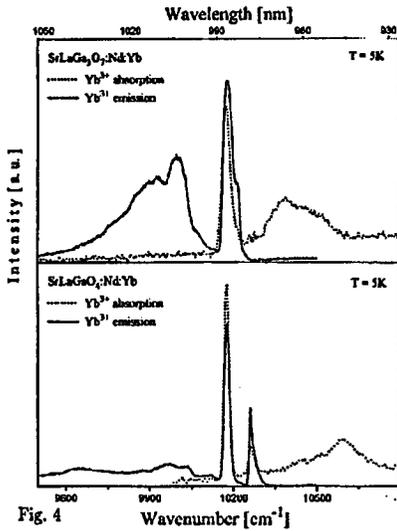


Fig. 4

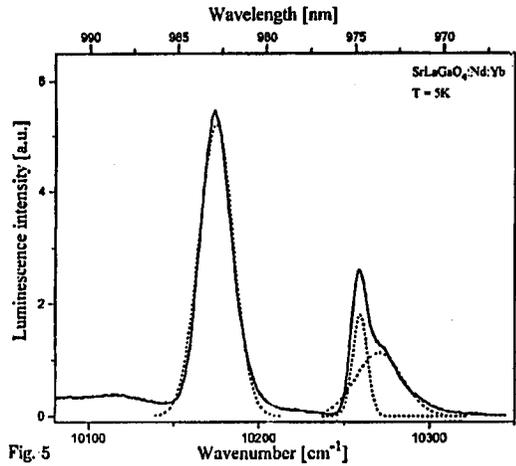


Fig. 5

Fig. 4. Yb^{3+} absorption and emission bands recorded at 5 K with $\text{SrLaGa}_3\text{O}_7$ and SrLaGaO_4 codoped with Nd^{3+} and Yb^{3+} .

Fig. 5. Details of Yb^{3+} emission in SrLaGaO_4 crystal codoped with Nd^{3+} and Yb^{3+} . Solid line represents the experimental bands. Dotted lines were obtained by numerical fit with Gaussian band shapes.

several nonequivalent sites. Two different Yb^{3+} sites in $\text{SrLaGa}_3\text{O}_7$ are indicated by asymmetric spectral lines showing a shoulder. In SrLaGaO_4 three nonequivalent Yb^{3+} sites may be derived from Fig. 5 which shows the details of low temperature emission bands. In both the matrices the most intense lines of Yb^{3+} emission are associated with transitions to the lowest crystal component of the ground $^2F_{7/2}$ multiplet. Thus, it appears that the materials investigated cannot be considered as promising for the design of low threshold ytterbium lasers.

5. Conclusions

Inhomogeneous broadening of Nd^{3+} emission band in SrLaGaO_4 is comparable to that recorded previously in SrLaGaO_4 and implies poor extraction efficiency. Emission intensity of Yb^{3+} in SrLaGaO_4 is concentrated in lines ending on the lowest crystal field component of the ground state. In $\text{SrLaGa}_3\text{O}_7$ the distribution of emission intensities is more favorable for a quasi-three-level laser action but the Stokes shift is rather low. In contrast to bigger rare earth ions the Yb^{3+} ions are situated in several different sites in both the lattices.

Acknowledgments

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