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Anisotropy of optical properties of $SrLaAlO_4$ and $SrLaAlO_4$:Nd

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Abstract

Single crystals of $SrLaAlO_4$ and $SrLaAlO_4$:Nd have been grown by the Czochralski method and their optical properties have been studied in polarized light. The crystals are positive uniaxial, and their birefringence is stable with respect to temperature in the 290 K–520 K temperature region. Undoped crystal is transparent from 240 nm to 7.6 μm. Intensities of absorption and spontaneous emission of Nd^{3+} are slightly lower for light polarized perpendicular than those for light polarized parallel to the optical axis. Laser action in $SrLaAlO_4$:Nd has been obtained for the first time using a diode laser as a pump. Stimulated emission occurs in the 1073 nm–1080 nm spectral region. Poor laser performance is attributed to the self-quenching of Nd emission.

Keywords: Anisotropy; Optical properties

1. Introduction

Some interest has been directed recently to the growth of the crystals of general chemical formula $ABCO_4$, where A denotes Ca or Sr, B denotes transition metals, yttrium or rare earth ions and C denotes Al or Ga [1–3]. The crystals have tetragonal symmetry, space group *I4/mmm*, and the dimensions of their unit cell make them suitable for application as substrates for high temperature superconductors. Crystal structure and some physical properties of several compounds belonging to the $ABCO_4$ family have been reported [4,5], but little is known about their optical properties. Unpolarized absorption and luminescence spectrum of single crystals of $CaYAlO_4$ doped with neodymium and erbium have been measured in the past [6]. More recently the crystal structure and spectroscopic properties of $CaNdAlO_4$ have been investigated [7]. It is ascertained that the $ABCO_4$ crystals are built up from translationally equivalent layers formed by CO_6 polyhedra and between the layers the ions denoted by A and B are distributed randomly in the sites of C_{4v} symmetry. The crystal structure of these compounds allows multiple doping with transition metals or rare earth ions. The rare earth ions replace substitutionally the ions denoted by B whereas transition metal ions replace substitutionally the ions denoted by C and are situated in slightly distorted octahedral sites. The interaction between different activators may provide an efficient sensitization of spontaneous and stimulated emission following optical excitation; therefore the crystals may be of interest as luminescent and laser materials. In this paper we report fundamental optical properties of undoped $SrLaAlO_4$ (SLA) and SLA doped with neodymium. Neodymium has been selected as an activator since Nd-doped crystals display the lowest threshold for laser action and are of practical interest as laser-active media.

2. Experimental details

La_2O_3 and Al_2O_3 of 99.99% and 99.999% purity and $SrCO_3$ not less than 99.95% purity were used. All chemicals were annealed in the standard conditions before weighing. The SLA compound was synthesized at 1200 °C in oxygen flow for 10 h before the crystal growth process. Crystal growth was performed by the Czochralski technique using r.f. induction heating with passive afterheater. An iridium crucible 50 mm high and 50 mm in diameter with the walls 1.5 mm thick was used. Crystals were pulled in an atmosphere of nitrogen containing about 1% oxygen. Seeds with the

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orientation (100) were used. Details concerning the crystal growth as well as anomalies of the growing process are described elsewhere [2]. Samples of SLA in the form of plates 0.2 mm thick were used for the measurement of fundamental absorption edges in the UV and IR regions of the spectrum. The samples were prepared with the optical axis (*c* axis) in the plane of the plates and the absorption was measured in light polarized parallel and perpendicular to the optical axis. A Varian model 2300 spectrophotometer was used in the visible and UV regions. The IR absorption was recorded with a Bruker model SFS 88 spectrophotometer.

Refractive indices were determined by the method of refraction in oriented prisms cut out from undoped SLA. An argon ion laser and a diode laser were used as sources of monochromatic light of wavelengths 457.9, 476.5, 488.0, 496.5, 501.7, 514.5 and 670 nm. The desired plane of polarization was selected by means of a quarter-wave plate followed by a Glan–Taylor polarizer. Accuracy of refractive index measurements is believed to be no worse than ∓0.0002. Polarized absorption and spontaneous emission spectra were recorded at room temperature for samples of SLA containing 1 at.% and 5 at.% neodymium. Spontaneous emission was excited by the 514 nm line of an argon ion laser and analysed by a 1 m grating monochromator equipped with a phase-sensitive detection system. The best quality sample of SLA containing 5 at.% neodymium has been selected for stimulated emission measurements. The sample in the form of a plate 2 mm thick with the *c* axis in the plane of the plate was placed in the planoconcave resonator near the plane parallel dichroic input mirror. Output mirrors with radius of curvature equal to 5 cm were used and the resonator length was adjusted so as to match the pump beam volume to the mode volume in the crystal. The active crystal was pumped longitudinally through the dichroic plane mirror by a nominally 3 W laser diode (model SDL 2482).

3. Results and discussion

3.1. Undoped $SrLaAlO_4$

Polarized absorption spectra of undoped SLA in the 5 μm–13.3 μm and in the 200 nm–450 nm spectral regions are shown in Fig. 1 and Fig. 2 respectively. Results of refractive index measurements are presented in Fig. 3 and the influence of temperature on refractive indices in the 290–520 K temperature region is presented in Fig. 4. Absorption in the IR begins at about 7.69 μm and forms strongly polarized bands associated with the composite lattice vibrations. On the basis of the analysis of IR spectra of $CaNdAlO_4$ [7] we may assign the bands peaking at 7.53 μm and 9.92 μm as two-phonon transitions. Measurements in the visible and UV revealed a broad absorption band stretching from about 500 nm to the UV absorption edge. This band, particularly prominent for the π-polarized spectrum, is associated probably with point defects which are created by the oxygen deficiency [2]. At about 240 nm the absorption coefficient rises abruptly forming an absorption edge, which is split by the crystal field. The highest measured absorption coefficient is only 200 cm^{-1}, and therefore the steep increase in absorption between 220 nm and 240 nm which is seen in Fig. 2 may be treated as a lower limit for the absorption edge of SLA.

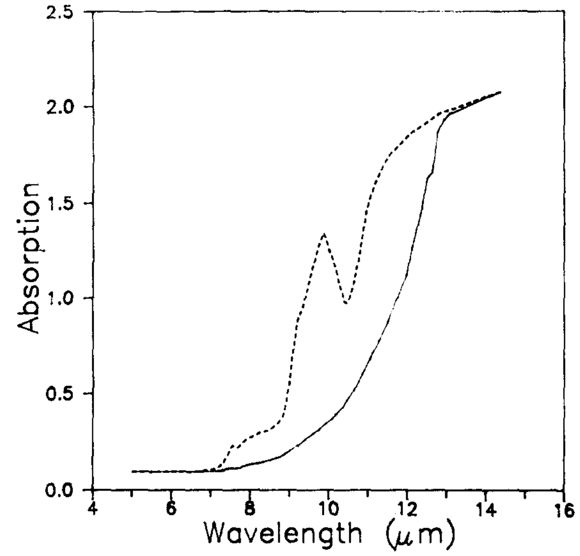

Fig. 1. Absorption of undoped SLA in the spectral region 5 μm–13.3 μm for light polarized parallel (——) and perpendicular (– – –) to the optical axis of the crystal.

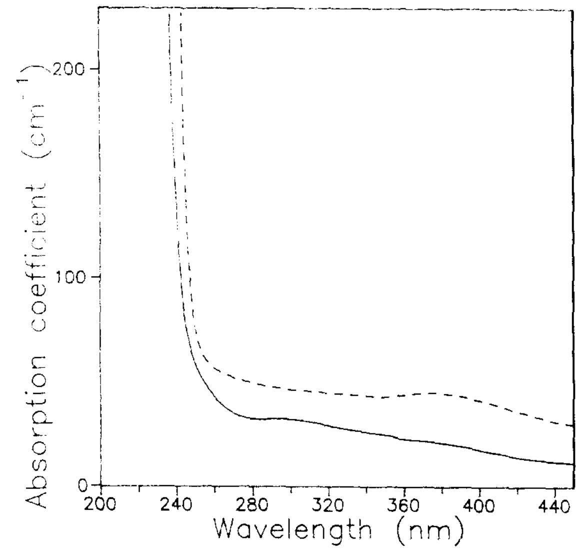

Fig. 2. Absorption spectra of undoped SLA recorded in the 200–450 nm spectral region for light polarized parallel (——) and perpendicular (– – –) to the optical axis of the crystal.

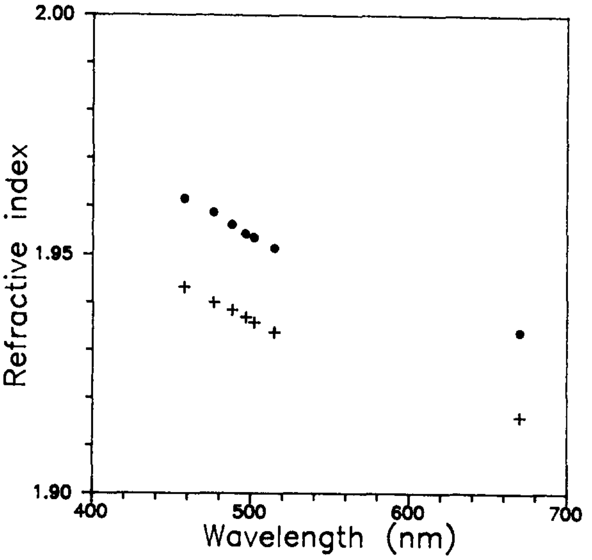

Fig. 3. Refractive indices vs. wavelength in the visible region for light polarized parallel (●) and perpendicular (+) to the optical axis of the crystal.

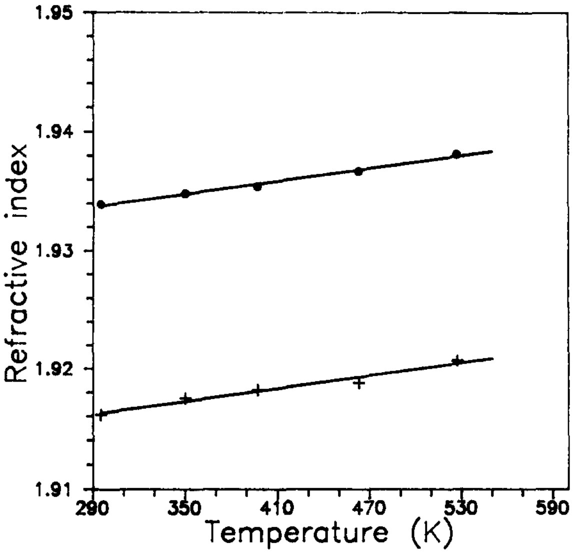

Fig. 4. Influence of temperature on refractive indices of undoped SLA for light polarized parallel (●) and perpendicular (+) to the optical axis of the crystal. ——, linear dependence at a rate $\Delta n/\Delta T = 1.8 \times 10^{-5}$ K^{-1}.

The data in Fig. 4 indicate that the birefringence of SLA crystals is stable with respect to temperature in the 290 K–520 K temperature region. Full lines in this figure follow a linear dependence with $\Delta n/\Delta T = 1.8 \times 10^{-5}$ K^{-1}.

The birefringence of SLA is sufficiently high to suppress the modification of the crystal anisotropy by thermally induced stresses which occur during optical pumping. Linearly polarized waves may propagate through the crystal without suffering depolarization. On the contrary, the variation in refractive indices with the temperature is rather marked and strong thermal lensing effects are expected.

3.2. *SrLaAlO$_4$ doped with neodymium*

Neodymium ions, although smaller than lanthanum ions, introduce additional disorder in the crystal structure of SLA, and the crystal growth of SLA:Nd becomes more demanding. All neodymium-containing samples obtained thus far look green because of a high density of point defects which absorb strongly in the UV and blue region of the spectrum. In Fig. 5 we present survey absorption spectra of SLA:Nd recorded at room temperature with the light perpendicular and parallel to the optical axis of the crystals. Assignments of absorption bands and corresponding oscillator strengths are given in Table 1. It can be seen that the overall intensities of transitions to excited multiplets do not differ considerably for the two polarizations; the intensities of individual transitions between the crystal field levels are merely distributed differently within the bands. One

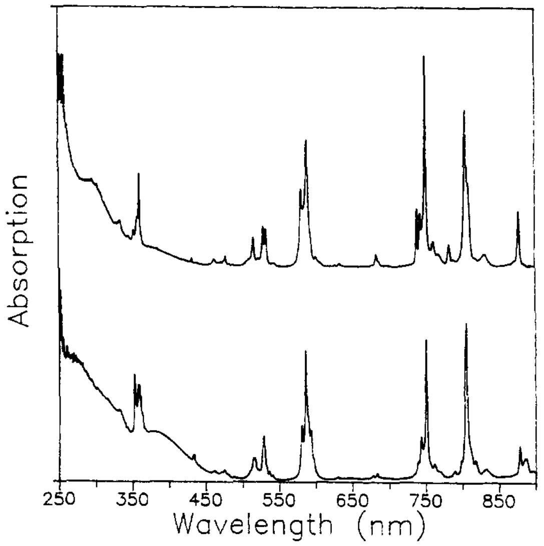

Fig. 5. Absorption spectra of SLA containing 5 at.% Nd recorded at room temperature with the light polarized perpendicular (lower spectrum) and parallel (upper spectrum) to the optical axis of the crystal.

Table 1

Oscillator strengths P_{exp} measured with the light polarized perpendicular (⊥) and parallel (∥) to the optical axis of the crystal: transitions are from the ground $^4I_{9/2}$ level to the level indicated

Excited level	Spectral region (nm)	$P_{exp} \times 10^6$ (∥)	$P_{exp} \times 10^6$ (⊥)
$^4F_{3/2}$	850–900	3.14	3.38
$^4F_{5/2}$, $^2H_{9/2}$	778–850	10.40	13.23
$^4F_{7/2}$, $^4S_{3/2}$	730–778	9.78	13.21
$^4F_{9/2}$	666–715	0.74	1.07
$^4G_{5/2}$, $^2G_{7/2}$	656–610	18.89	21.16
$^2K_{13/2}$, $^4G_{9/2}$, $^4G_{7/2}$	497–555	9.51	10.65

can note that the absorption bands are relatively large but almost all of them are dominated by a few narrow and intense lines. This feature is not advantageous for optical pumping with classical sources such as xenon or krypton lamps. Also, in the case of optical pumping with laser diodes a stringent control of laser diode temperature may be necessary, since the spectrum corresponding to the $^4I_{9/2}$–$^2H_{9/2}$, $^4F_{5/2}$ transition at about 800 nm, commonly used as a pump band, is predominantly concentrated in a narrow spectral region (800 nm–810 nm). In contrast to absorption spectra the luminescence spectra associated with the $^4F_{3/2}$–$^4I_{9/2}$ and $^4F_{3/2}$–$^4I_{11/2}$ transitions are relatively broad. The polarized luminescence band associated with the latter transition is shown in Fig. 6. The broader the luminescence band, the lower is the value of stimulated emission cross-section, and therefore the threshold for laser action is expected to be higher than in ordered neodymium-doped crystals. Measurements of the stimulated emission have been made in order to examine the predictions derived from spectroscopic investigation. In Fig. 7 we present the dependence of output power of the SLA:Nd laser on absorbed pumping power for several different output mirror transmissions. The highest optical slope efficiency of 16% has been obtained for 3% transmission. Poor laser performance is not due to low optical quality of the crystal because the Findlay–Clay plot indicates losses close to 0.02 cm^{-1}. A more probable reason is low quantum efficiency of the $^4F_{3/2}$ level as indicated by the reduction in luminescence lifetime by a factor of 2 when the Nd concentration increases from 1 at.% to 5 at.%. The influence of laser diode temperature on normalized output power of the SLA:Nd laser is shown in Fig. 8. As expected from an analysis of absorption spectra the laser output depends strongly on the pump wavelength which shifts by about 0.3 nm/°C. It has been found that the stimulated emission occurs in the 1073 nm–1080 nm spectral region.

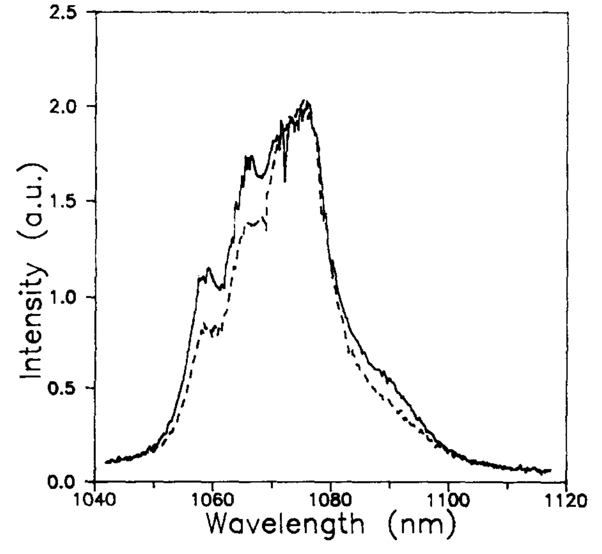

Fig. 6. Luminescence band associated with the $^4F_{3/2}$–$^4I_{11/2}$ transition polarized parallel (——) and perpendicular (– – –) to the optical axis of the crystal.

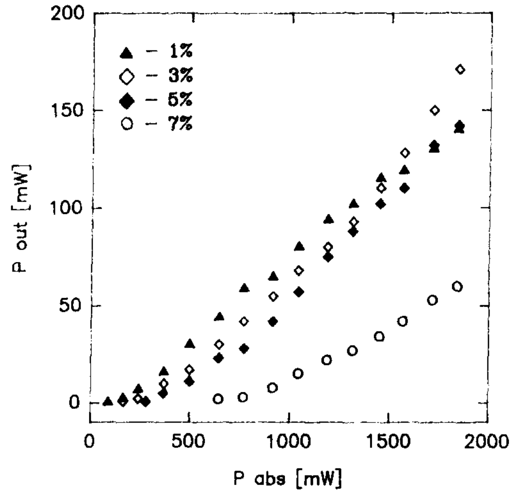

Fig. 7. Output power P_{out} of SLA:Nd laser vs. absorbed pumping power P_{abs} for different output mirror transmissions.

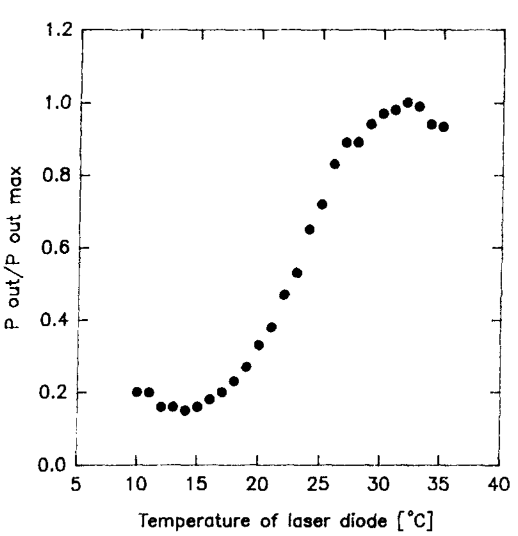

Fig. 8. Normalized output power of SLA:Nd laser vs. temperature (wavelength) of pumping laser diode.

4. Conclusions

SLA forms optically positive uniaxial crystals which are transparent from 240 nm to 7.6 μm. Refractive indices of the crystal are influenced markedly by temperature, and therefore strong thermal lensing effects resulting from the non-uniform temperature distribution should be accounted for in practical application. SLA may be doped with rare earth ions but the stability of doped crystals is reduced. Laser action in SLA:Nd has been achieved with laser diode pumping; however, the spectral properties of this ion–host combination are not very promising because of narrow absorption bands and relatively broad emission bands.

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