Growth and spectroscopic preliminary investigations of Sm^{3+} doped strontium hexa-aluminates single crystals

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Strontium lanthanum hexa-aluminates crystals (ASL) doped with Sm^{3+} with formula $Sr_{1-x}Sm_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ are investigated for lasers operating in visible spectral range. The crystal with compositional parameters x = 0.2 and y = 0.05 have been grown by the Czochralski pulling technique. High resolution optical absorption and emission spectra at 10K and room temperature were recorded. Preliminary investigations of spectroscopic properties of Sm^{3+} doped ASL crystal were carried out.

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1. Introduction

Extensive development of diode pumped solid state lasers continuously triggers the search for new laser active materials. In particular, laser systems operating in visible domain are of great practical interest in various fields of applications including medicine, information processing and display, materials processing, etc. Actually, there are very few laser materials with efficient emission in visible, and accessible wavelengths are very limited. Examples of these lasers are limited to those based on Pr^{3+} ions and to accordable lasers (Cr: $BeAl_2O_4$, Cr: Mg_2SiO_4, LiSAF: Cr, Ti: Sapphire) which cover a very small domain of visible laser emissions (maximum 100 nm in the case of Ti: Sapphire lasers).

Sm^{3+} ion with electronic configuration $4f^5$ has a complex energy level scheme and presents a variety of transitions between 4*f* levels. The emission spectrum of samarium is dominated by transitions from the $^4G_{5/2}$ excited level located at about 17500 cm^{-1} [1]. Due to the large energy gap of about 7000 cm^{-1} to the next lower level, $^4G_{5/2}$ decay is predominantly radiative. The strongest emission is observed in the red part of the spectrum. Laser action in the visible domain, corresponding to $^4G_{5/2} \rightarrow {}^4H_{7/2}$ transition was observed at 617 nm for Sm: YAG [2], 610 nm for $LiNbO_3$: Sm [3], 594 nm for Sm: $SrAl_{12}O_{19}$ [4] and 613 nm for (Ca, Mg, Zr) GGG: Sm [5]. Sm^{3+} presents large absorption cross sections for wavelength pumping in visible (350 - 550 nm domain) and IR (~ 940 nm domain) accesible for Argone laser and InGaAs laser diodes, efficient laser sources current marketed. Most of the recent investigations are focused on providing of Sm^{3+} ion based phosphors with efficient luminescence [6-9].

A very interesting class of partially disordered crystal with typical magnetoplumbite structure of $PbFe_{12}O_{19}$ (MP), $P6_3/mmc$ spatial group) is strontium lanthanum and magnesium hexa-aluminates doped with trivalent rare earth ions - $Sr_{1-x}RE_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ (ASL: RE) where $0 < x < 1$ and $y \leq x$. Global research effectuated until now on ASL: RE laser materials with partially disordered structure type were limited at only two such systems: $Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ (ASL: Nd) and $Sr_{1-x}Pr_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ (ASL: Pr).

The first investigations on $Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ crystals were dedicated to finding the best compositions to allow congruent melting of the compounds and also to avoid Nd^{3+} quenching emission. ASL: Nd crystals with different compositions were grown from melt (melting point ≈ 1850°C) by Czochralski method and it was found that the melt and growth processes of crystals depend on the compositional parameter x [10, 11]. The spectroscopic investigations highlighted the strong shift to higher $^4F_{3/2}$ Nd^{3+} energy levels in Nd: ASL crystals, permitting to obtain laser emission at 900 nm of Nd^{3+}, Ti: Sapphire pumped at 790 nm [12]. Until now, this is the shortest laser emission wavelength obtained in laser materials doped with Nd^{3+} ions (at room temperature in cw). Also, in ASL: Nd crystals efficient laser emission was obtained in the range of 1 μm (corresponding to $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition), by laser diode pumping [13].

$Sr_{1-x}Pr_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ - (ASL: Pr) compounds were firstly investigated as phosphorus for Xe lamps, based on ultraviolet-visible quantum cutting by energy transfer. ASL: Pr materials were also investigated as laser materials. Similar to ASL: Nd crystals, high resolution spectroscopic investigations on $Sr_{1-x}Pr_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ crystals with extended range of compositions revealed the presence of two types of Pr^{3+} non-equivalent centers. Based on the correlation of spectral data with crystal structure, structural models for these two non-equivalent centers were elaborated [14, 15]. The existence of two quantum process in the visible emission from the ultraviolet was also demonstrated [16].

This paper present the preliminary investigations on crystal growth and spectroscopic properties of $Sr_{1-x}Sm_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ crystal with compositional parameters x = 0.2 and y = 0.05.

2. Experimental

To synthesize $Sr_{0.2}Sm_{0.05}La_{0.15}Mg_{0.2}Al_{11.8}O_{19}$ - ASL: Sm (5 at%) compound, solid state reaction technique was used. ASL: Sm (5 at%) single crystal was grown using the conventional radio frequency (RF) heating Czochralski method from iridium crucibles under nitrogen atmosphere. The optical spectroscopic measurements of ASL: Sm (5 at%) single crystal were performed on an extended spectral range from 350 to 1600 nm. The absorption spectra were recorded with a setup consisting of a Jarell Ash monochromator, S20 and S1 photomultipliers, Si and Ge photodiodes and a Lock-in amplifier on line with a computer. The emission spectra were obtained by non - selective excitation with Xe lamp. A closed cycle He refrigerator was used for low temperature measurements.

3. Results and discussions

The solid state reaction technique was adopted to obtain $Sr_{0.2}Sm_{0.05}La_{0.15}Mg_{0.2}Al_{11.8}O_{19}$ single phase compound. 99.99% purity chemicals of $SrCO_3$, $MgCO_3$, La_2O_3, Sm_2O_3 and α-Al_2O_3 were used as starting materials. In order to eliminate the absorbed water, the La_2O_3 and Sm_2O_3 powders were preheated at 1000°C for 12 h, and $SrCO_3$ and $MgCO_3$ powders where preheated at 400°C for 10 h. Then, the compounds were weighed according to their formulas, mixed by grinding and cold-pressed into cylindrical pellets with dimensions of 30 mm in diameter and about 40 mm in length. The pellets were prereacted by heating at 950°C for 15 h in order to decompose the carbonates. Subsequently, these pellets were crushed, mixed and pressed again into pellets with the same dimensions and annealed for 36 h at 1550 °C.

Single crystal of $Sr_{0.2}Sm_{0.05}La_{0.15}Mg_{0.2}Al_{11.8}O_{19}$ was grown by Czochralski method. The growth was performed by pulling from melt contained in an iridium crucible of 30 mm diameter and 30 mm height, in a continuous N_2 flow. The growth temperatures, determined by an infrared pyrometer, were about 1850 ± 15°C. The temperature gradient just above the melt was 30 - 40°C/cm. In order to avoid the formation of polycrystals in the growth process, preheating at a temperature of 50-60°C higher than the melting point was required. Then, the temperature was reduced to the growth temperature. The pulling rate was 0.6 – 0.8 mm/h at a rotation rate of 25 rpm. The crystal was cooled to room temperature at a rate of 40 ºC/h. One sample exerted from ASL: Sm (5 at%) grown crystal is shown in Fig. 1.

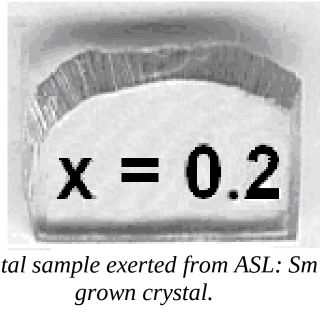

Fig. 1. Crystal sample exerted from ASL: Sm (5 at%) grown crystal.

$Sr_{0.2}Sm_{0.05}La_{0.15}Mg_{0.2}Al_{11.8}O_{19}$ crystal has a partially disordered structure, typical to magnetoplumbite $PbFe_{12}O_{19}$ (MP), $P6_3/mmc$ spatial group). Large ions as Sr^{2+} and Ln^{3+} (Sm, La) occupy cations positions of Pb^{2+} *(2d)* with D_{3h} symmetry, while smaller cations Al^{3+} enter in positions of Fe^{3+} of magnetoplumbites structure. Ln^{3+} ions can substitute only large Sr^{2+} ions and they have in near neighbors 12 O^{2-}. Partially disordered structure comes from the fact that Sm^{3+} ions have in the first cationic vicinity 6 Pb^{2+} available cationic positions which can be randomly occupied by Ln^{3+} and Sr^{2+} ions, leading to appearance of non-equivalent centers (different neighborhoods of Sm^{3+} active ion). Low density of Pb^{2+} positions of magnetoplumbite (~3.38 10^{19} ioni/ cm^3) require a relatively high concentration of Sm^{3+} for efficient pumping, limited by quenching.

The room temperature and 10K absorption spectra of Sm^{3+} in $Sr_{1-x}Sm_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ (x = 0.2, y = 0.05) corresponding to the $^6H_{6/2}\rightarrow{}^6F_{7/2}$ transitions were measured in unpolarized light with beam propagation along the $\vec{c}$ axis, as is illustrated in Fig. 2.

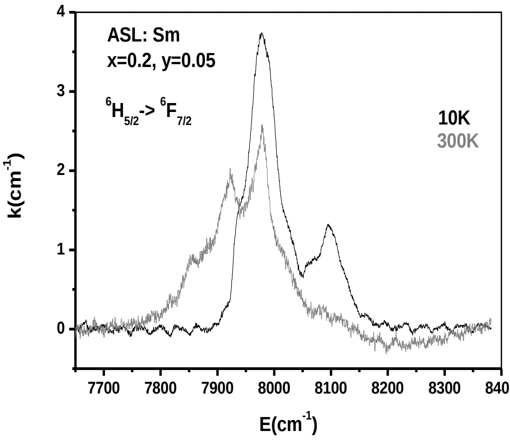

Fig. 2. Absorption spectra at 10 and 300K of Sm: ASL corresponding to the $^6H_{6/2} \rightarrow {}^6F_{7/2}$ transitions.

Comparing ASL: Sm (5 at%) with YAG: Sm (1 at%) absorption spectra for the same transition $^6H_{5/2}\rightarrow{}^6F_{7/2}$ (Figure 3), it can be seen that in the case of YAG: Sm (1 at%) there are 4 narrow lines while for ASL: Sm (5 at%) crystal there are only two wide absorption lines due to the mixed occupancy with Sr^{2+} and Ln^{3+} (Sm and La) ions of *2d* cations positions, which suggest the existence of nonequivalent structural centers.

The emission spectra obtained by non-selective excitation with Xe lamp were measured at room temperature and 10 K. The visible and i.r. emissions are illustrated in Fig. 4 and represent the emission corresponding to $^4G_{5/2} \rightarrow {}^4H_J$ transitions. The manifold $^4G_{5/2}$ level is the only one emitting level of Sm^{3+} ion. The emission lines are unsolved and have asimetric shape. The asymmetry suggests the presence of two or more very close emission lines.

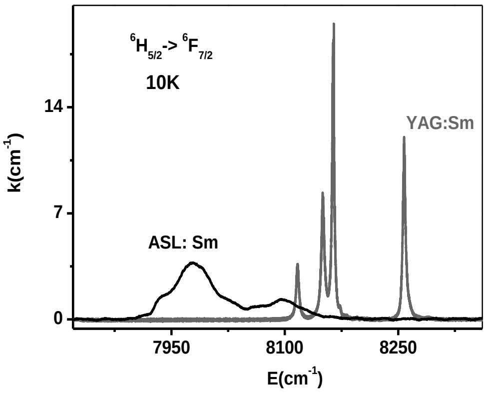

Fig. 3. Absorption spectra at 10K of Sm doped in ASL comparing with Sm doped YAG corresponding to $^6H_{5/2} \rightarrow {}^6F_{7/2}$ manifold transition.

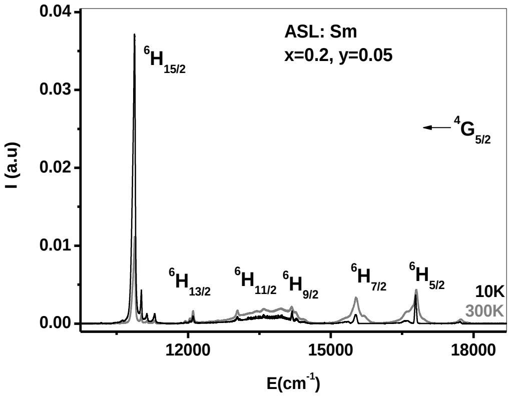

Fig. 4. Emission spectra at 10 and 300K of Sm doped ASL corresponding to $^4G_{5/2} \rightarrow {}^4H_J$ manifold transitions.

4. Conclusions

Single crystal of $Sr_{1-x}Sm_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ with compositional parameters x = 0.2 and y = 0.05 was grown by conventional Czochralski technique. The preliminary absorption spectra on ASL: Sm (5 at%) crystal confirm that the complex chemical composition of ASL determines multiple possibilities of occupation of the cationic sites, inducing strong structural disorder that could influence the spectroscopic and laser emission properties of the Sm^{3+} ions. These preliminary results motivate the further research on $Sr_{1-x}Sm_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ crystals with different compositional parameters, in order to obtain solid state lasers with emission at new wavelengths in visible domain.

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