

Growth and characterization of Nd³⁺ doped strontium hexa – aluminates single crystals

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Nd³⁺-doped strontium hexa-aluminates crystals, Nd: ASL (Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O₁₉), with an extended composition parameter x (0.05 and 0.5), have been grown by the Czochralski pulling technique. Structural and compositional properties of the as-grown crystals have been studied. The results show that high crystalline perfection and large size crystals of both compositions can be grown. Low-temperature optical absorption spectra of crystals with compositions corresponding to $x = 0.5$ and $x = 0.05$ reveal that such crystals predominantly contain either C₁- or C₂-type Nd³⁺-centers respectively. The possibility to thus differentiate between the two types of the dopant structural centers is of utmost importance for laser applications.

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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, diode-pumped solid state lasers operating in the blue range are of interest for various applications including high-density data storage, phototherapy, medical diagnosis, etc. Such a device can be realized using a neodymium-doped laser material operating on the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ laser transitions, with subsequent doubling in a non-linear crystal. For instance, a laser at 473 nm [1] has been obtained by frequency doubling the 946 nm emission of the Nd: YAG laser. An extension towards higher energies has been reported for neodymium-doped strontium lanthanum aluminate crystals, ASL: Nd (Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O₁₉): continuous-wave laser emission at a very short laser wavelength, 900 nm, with a slope efficiency of ~60% has been achieved [2].

Strontium lanthanum aluminate doped with Nd³⁺ ions is a laser material formed by partial replacement of Sr²⁺ ions by Nd³⁺ and La³⁺ in the uniaxial magnetoplumbite-type (MP) structure of strontium hexaaluminate, SrAl₁₂O₁₉, belonging to the symmetry space group P6₃/mmc. The crystal's electroneutrality is restored by partial replacement of Al³⁺ ions by Mg²⁺, leading to the general formula Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O₁₉ (where $0 < x < 1$ and $y \leq x$). It has been found that introduction of La³⁺ ions improve the crystal quality. The optically inert La³⁺ ions assure a large range of compositional parameter x , the Nd³⁺ content being limited to $0.05 \leq y \leq 0.15$ due to concentration quenching of fluorescence [3, 4].

Previous crystal growth studies of ASL: Nd have revealed that the tendency to grow along the \bar{c} direction (preferred for laser action) and congruent melting are connected with the strontium content [5]. Thus, the higher is the Sr²⁺ content, the easier is the \bar{c} axis growth, but at the same time the melting of the compound is no longer

congruent. Therefore, it has been implied that the useful range of compositions is limited to $x = 0.2 \div 0.4$.

The spectral studies have been focused on the determination of global spectral parameters necessary for evaluating this laser system and determining the optimum compositions and Nd³⁺ concentration [3-6]. A single center model has been adopted. Recent high-resolution optical spectroscopy investigations have revealed a two-center structure dependent on the composition [7]. The spectral characteristics (energy levels, emission kinetics) of the two centers, C₁ and C₂, are quite different. Emission intensity associated with the C₁ centers increases with x , while that of C₂ centers decreases. Since crystals with an intermediate composition $0.2 < x < 0.4$ contain both centers, their use may lead to instability in laser emission. A dependence of laser parameters on the composition parameters x in the 0.2 – 0.4 range has been observed [5]. It is desirable to have samples with one prevailing center, and for this purpose growth of ASL: Nd crystals with an extended x -range toward smaller and larger values is considered. The larger values are limited by the possible changes in crystal structure; it is known that for $x = 1$ the crystal has a different structure [8].

This paper presents results of crystal growth of Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O₁₉ with the extended x -range ($x = 0.05$ and $x = 0.5$) for the same Nd³⁺ content ($y = 0.05$) in the synthesized materials. The compositions of the grown crystals have been determined, and X-ray diffraction measurements have been carried out to characterize the structural changes with composition. Low-temperature high-resolution spectroscopic investigation has been performed to analyze the influence of composition of ASL: Nd crystals on the spectral properties.

2. Experimental

To synthesize the neodymium-doped strontium lanthanum aluminate material (Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O₁₉),

the solid state reaction technique was used. Single crystals of ASL: Nd were grown using the conventional radio frequency (RF) heating Czochralski method from iridium crucibles under nitrogen atmosphere. Phase identification and determination of lattice parameters of the sintered materials and of the grown crystals were performed using a Siemens D5000 diffractometer with Co K α radiation ($\lambda = 1.78897 \text{ \AA}$). Compositional analyses of the grown crystals were carried out by the central service of the microanalysis of CNRS (Centre National de la Recherche Scientifique) from Vernaison, France. For optical spectra measurements a high-resolution monochromator (0.3 cm^{-1} resolution) and a photon counter in conjunction with a multichannel analyzer Turbo-MCS for detection were used.

3. Results and discussion

Since the phase diagram of ASL: Nd was not reported in the literature, the solid state reaction technique was adopted to obtain $\text{Sr}_{0.5}\text{Nd}_{0.05}\text{La}_{0.45}\text{Mg}_{0.5}\text{Al}_{11.5}\text{O}_{19}$ and $\text{Sr}_{0.95}\text{Nd}_{0.05}\text{Mg}_{0.05}\text{Al}_{11.95}\text{O}_{19}$ single phase compounds. 99.99% purity chemicals of SrCO_3 , MgCO_3 , La_2O_3 , Nd_2O_3 and $\alpha\text{-Al}_2\text{O}_3$ were used as starting materials. In order to eliminate the absorbed water, the La_2O_3 and Nd_2O_3 powders were preheated at $1000 \text{ }^\circ\text{C}$ for 12 h and SrCO_3 , MgCO_3 powders at $400 \text{ }^\circ\text{C}$ for 10 h. Then, the compounds were immediately weighed according to their formulas, mixed by grinding and cold-pressed into cylindrical pellets with dimensions of 45 mm in diameter and 120 mm in length. The pellets were prereacted by heating at $950 \text{ }^\circ\text{C}$ 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 $1550 \text{ }^\circ\text{C}$.

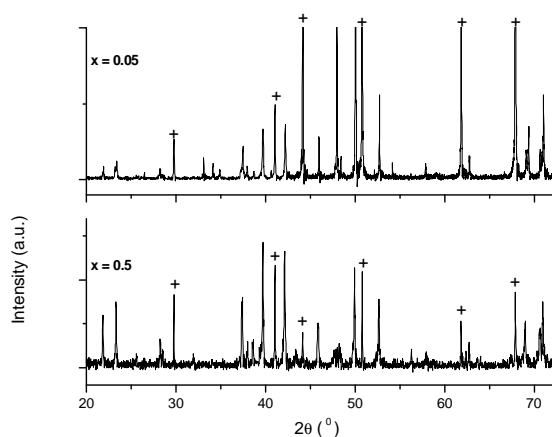


Fig. 1. X-ray powder diffraction patterns on synthesized $\text{Sr}_{0.5}\text{Nd}_{0.05}\text{La}_{0.45}\text{Mg}_{0.5}\text{Al}_{11.5}\text{O}_{19}$ and $\text{Sr}_{0.95}\text{Nd}_{0.05}\text{Mg}_{0.05}\text{Al}_{11.95}\text{O}_{19}$ materials. Six peaks marked with a '+' sign belong to the parasitic $\alpha\text{-Al}_2\text{O}_3$ phase.

X-ray powder diffraction patterns of the synthesized products were taken to examine whether the solid state reactions were complete. The patterns of Fig. 1 show that

the synthesized products are not single phases of $\text{Sr}_{1-x}\text{Nd}_y\text{La}_{x-y}\text{Mg}_x\text{Al}_{12-x}\text{O}_{19}$, with $x = 0.05$ and 0.5 , $y = 0.05$. Both samples contain an extra phase of $\alpha\text{-Al}_2\text{O}_3$ (Corundum, syn.). The six most intense lines are characteristic of $\alpha\text{-Al}_2\text{O}_3$ ($a = 4.758 \text{ \AA}$, $b = 12.991 \text{ \AA}$ in the hexagonal system, space group $R\bar{3}c$) [9], and they are marked with a '+' sign. The full synthesis of both compounds occurs during premelting in the crucible.

Single crystals were grown by the Czochralski technique with RF heating and diameter control by differential weighing of the growing crystal. The growth was performed by pulling from melt contained in an iridium crucible of 50 mm diameter and 50 mm height, in a continuous N_2 flow. The growth temperatures, determined by an infrared pyrometer, were about $1850 \pm 15 \text{ }^\circ\text{C}$. The temperature gradient just above the melt was $30\text{-}40 \text{ }^\circ\text{C}/\text{cm}$. In order to avoid the formation of polycrystals in the growth process, preheating at a temperature $50\text{-}60 \text{ }^\circ\text{C}$ higher than the melting point was required. Then, the temperature was reduced to the growth temperature. In all growth processes we used rectangular $\langle 001 \rangle$ oriented single crystalline seeds with dimensions of $5 \times 5 \times 30 \text{ mm}^3$. The pulling rate was $0.5 - 1 \text{ mm/h}$ at a rotation rate of 25 rpm. Both crystals were cooled to room temperature at a rate of $40 \text{ }^\circ\text{C}/\text{h}$.

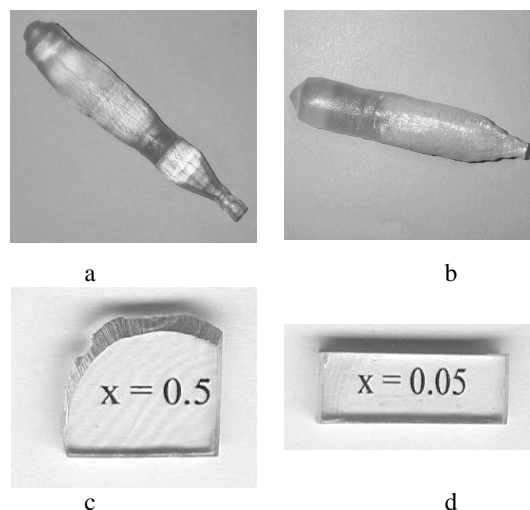


Fig. 2. Photographs of as-grown ASL: Nd crystals with $x = 0.5$ and $x = 0.05$ in the synthesized materials (a and b respectively) and of the corresponding cleaved samples (c and d).

Immediately after seeding the ASL: Nd crystal with $x = 0.5$ starting composition maintains the seed direction, but during the shouldering process the initial direction is changed into a new growth direction, deviated by approximately 40° with respect to the \bar{c} axis. The as-grown crystal is shown in Fig. 2a. It is of good crystalline quality and has a size of 20 mm in diameter and 80 mm in length. The ASL: Nd crystal with $x = 0.05$ starting composition, shown in Fig. 2b, is half polycrystalline (initially grown part) followed by a good single crystalline part.

X-ray powder diffraction patterns of samples exerted from the polycrystalline part, single crystal and the

residual melt are shown in Fig. 3. A small amount of the parasitic α -Al₂O₃ phase exists only in the polycrystalline part.

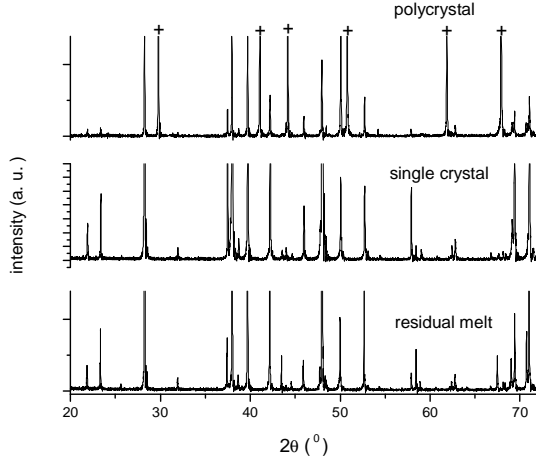


Fig. 3. X-ray powder diffraction patterns of the $Sr_{0.95}Nd_{0.05}Mg_{0.05}Al_{11.95}O_{19}$ (starting composition) crystal from polycrystalline part, single crystal part and residual melt. Peaks marked with a '+' sign are characteristic of the parasitic α -Al₂O₃ phase.

The occurrence of the parasitic phase arises from noncongruent melting of the $Sr_{0.95}Nd_{0.05}Mg_{0.05}Al_{11.95}O_{19}$ synthesized material [5]. The absence of another parasitic phase, to compensate for the α -Al₂O₃ segregation, indicates that an aluminum deficit with respect to the stoichiometric composition exists in the grown crystal. In the single crystalline part, no parasitic phase is observed, and the crystal is of good quality. This implies that the melt becomes congruent after segregation of the parasitic phase in the polycrystalline part. The spontaneous growth direction of the single crystal part is very close to the growth direction preferred by the ASL: Nd crystal with $x = 0.5$.

From the X-ray powder diffraction patterns of ASL: Nd single crystals grown from the synthesized materials with $x = 0.5$ and $x = 0.05$, we have calculated the unit cell parameters for both crystals. The lattice parameters and chemical compositions of the grown crystals are given in Table 1.

Table 1. Chemical composition and lattice parameters of ASL: Nd³⁺ single crystals.

Starting Composition	Formulas deduced from compositional analyses	Lattice parameters (± 0.002 Å)
$Sr_{0.5}Nd_{0.05}La_{0.45}Mg_{0.5}Al_{11.5}O_{19}$ ($x = 0.5, y = 0.05$)	$Sr_{0.492}Nd_{0.048}La_{0.453}$ $Mg_{0.443}Al_{11.542}O_{19}$	$a = b = 5.577$ $c = 21.987$
$Sr_{0.95}Nd_{0.05}Mg_{0.05}Al_{11.95}O_{19}$ ($x = 0.05, y = 0.05$)	Single Crystal Part: $Sr_{0.941}Nd_{0.059}$ $Mg_{0.076}Al_{11.929}O_{19}$	$a = b = 5.566$ $c = 21.996$
	Polycrystalline part: $Sr_{0.945}Nd_{0.051}Mg_{0.011}Al_{11.979}O_{19}$	

The ASL: Nd crystals have been cleaved perpendicularly to the \vec{c} axis, and good quality samples suitable for spectroscopic or laser investigations have been obtained. Figs. 2c and 2d show the samples cleaved from both grown crystals.

The complex composition of ASL: Nd crystals and the distribution of various cations in specific sites (La³⁺ and/or Nd³⁺ in Sr²⁺ sites and the charge compensating ion Mg²⁺ in the trivalent Al³⁺ cationic sublattice) can induce a large variety of non-equivalent Nd³⁺ ions sites exhibiting different optical spectra. The presence of two basic structural centers of Nd³⁺ in ASL, with different static and dynamic spectral characteristics, has been reported recently [10]. The relative intensities of absorption bands associated with these centers are composition dependent: the intensity of C₁ absorption band increases with the composition parameter x , while the intensity of C₂ absorption band decreases.

The low temperature (15 K) absorption spectra of Nd³⁺ in $Sr_{1-x}Nd_xLa_{x-y}Mg_xAl_{12-x}O_{19}$ ($x = 0.05$ or 0.5 , $y = 0.5$) measured in unpolarized light with beam propagation along the \vec{c} axis show important differences between the two samples in terms of the ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$ transitions. This is illustrated in Figs. 4a and 4c. For comparison with previously published data [7, 10], the absorption of a sample with $x = 0.2$ is added in Fig. 4b.

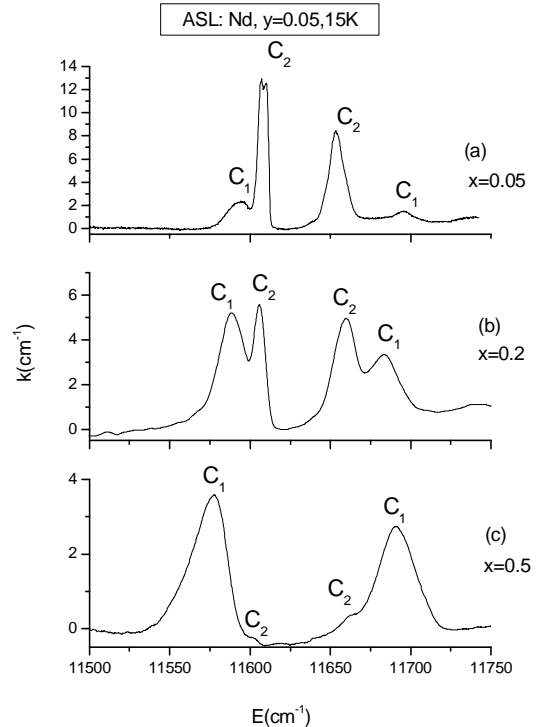


Fig. 4. Absorption spectra at 15K of Nd³⁺-centers in $Sr_{1-x}Nd_xLa_{x-y}Mg_xAl_{12-x}O_{19}$ with (a) $x = 0.05$, (b) $x = 0.2$ and (c) $x = 0.5$ corresponding to the ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$ transitions manifold.

The absorption spectra confirm the existence of two structural centers, C₁ and C₂, and the advantageous

evolution of their relative absorption intensities with composition.

4. Conclusions

Single crystals of Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O₁₉ (with x = 0.05, 0.5 and y = 0.05 starting compositions) of good quality and large dimensions were grown by the conventional Czochralski technique. The main problem associated with the Sr_{0.95}Nd_{0.05}Mg_{0.05}Al_{11.95}O₁₉ crystal is that the grown crystal contains, only at the beginning, a polycrystalline part. However, this initially grown part is followed by a good quality single crystalline part of sufficient size for laser applications.

The absorption spectra on ASL: Nd crystals with extended x-range toward smaller and larger values, beyond the range proposed previously (x = 0.2 ÷ 0.4), confirm that by a proper choice of compositional parameter x, crystals in which one of the Nd³⁺ structural centers is dominant can be obtained (C₁ for x = 0.5 and C₂ for x = 0.05).

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