LANTHANIDE-MAGNESIUM ALUMINOGALLATES, PROMISING LASER MATERIALS

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LANTHANIDE-MAGNESIUM ALUMINOGALLATES, PROMISING LASER MATERIALS

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Abstract

The purpose of this work is to increase the power of the lanthanum-neodymium-magnesium hexaaluminate "LNA" laser emission. When Ga is substituted for Al the unit cell parameters and consequently the Nd-O distances increase, therefore crystal field experienced by Nd^{3+} and fluorescence quenching decrease. It is then possible to increase the concentration of the Nd^{3+} activators ions in the laser crystals.
Synthesis, composition domain, optical properties and crystal growth of lanthanum-neodymium aluminogallates with a magnetoplumbite-like structure are described.

Introduction

Lanthanum-neodymium hexaaluminate $La_{1-x}Nd_xMgAl_{11}O_{19}$, "LNA", is a very promising high power laser material able to compete with Nd:YAG in most of its applications (1-3). But Nd^{3+} concentration, N, and consequently laser emission power, are limited for this compound because of the quenching of the fluorescence which appears for values of N above ~ 0.3 10^{21} $Nd^{3+}cm^{-3}$.
F. Auzel showed that lower is the crystal field experienced by Nd^{3+}, lower is the fluorescence quenching (4). Therefore it might be possible to decrease this phenomena by increasing the unit cell parameters, leading to a lengthening of the neodymium-oxygen distances. Partial or total Al replacement by Ga, whose ionic radius is higher, could be a solution. Consequently, compounds with formula $(La_{1-x}Nd_x)_{1-z/3}Mg_{1-z}(Ga_{1-v}Al_v)_{11+z}O_{19}$ have been synthesized and studied.

Solid solution

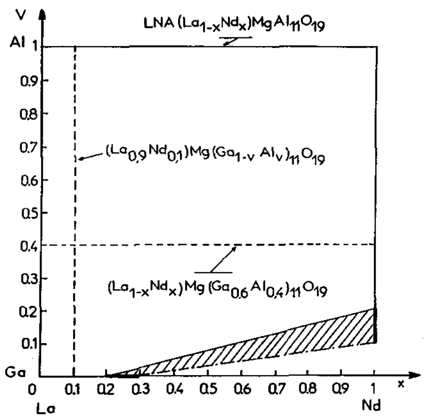

Figure 1
Composition domain of aluminogallates $(La_{1-x}Nd_x)Mg(Ga_{1-v}Al_v)_{11}O_{19}$.
The true limit of the MP phase is a line located in the hatched area.

Composition domain have been determinated for z = 0.
$(La_{1-x}Nd_x)Mg(Ga_{1-v}Al_v)_{11}O_{19}$ phases have been synthesized by heating a mixture of oxides at high temperatures (1400-1550°C). The solid solution which forms belongs to the magnetoplumbite (MP) structural type. For 0 ⩽ Ga ⩽ 85 at % (v ⩾ 0.15), x can be varied continuously from 0 to 1. But when v < 0.15, the MP single phased domain becomes narrower and, for v = 0, the Nd^{3+} solubility in the pure gallate is limitated to x ~ 0.25 (Fig. 1). For constant x, unit cell parameters increase with gallium ratio but do not exhibit a linear dependence on composition. Distribution of Al and Ga among the various cationic sites is not statistical, as indicated also by a ^{27}Al MAS-NMR investigation (5,6).
Al and Ga have a strong preference for respectively octahedral and tetrahedral sites in the structure

Optical properties

Optical properties of solid solution have been studied for powders with formula $(La_{1-x}Nd_x)Mg(Ga_{0.6}Al_{0.4})_{11}O_{19}$. This composition was choosen because on the one hand the solid solution is total and exists for all the x values and, on the other hand, it must be representative of the gallium contribution (0.6 Ga for 0.4 Al). The Nd^{3+} fluorescence intensity I_f ($^4F_{3/2}$ - $^4I_{9/2}$ transitions) varies with Nd^{3+} content (Fig. 2).

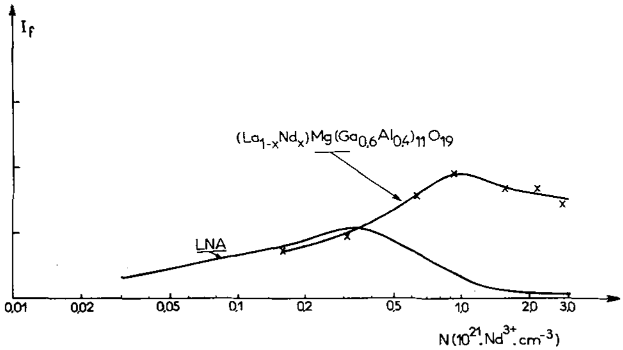

Figure 2
Variation of the fluorescence intensity I_f according to the Nd^{3+} content of an aluminogallate and comparison with "LNA".

Comparison with results obtained for LNA shows that

- the maximum of fluorescence intensity is two times higher for aluminogallate
- I_f reaches its maximum for three times as much Nd^{3+}. Quenching of fluorescence appears only for $N > 10^{21}$ Nd^{3+} cm^{-3}.

Furthermore, Nd^{3+} $^4F_{3/2}$ fluorescence lifetime for aluminogallate decays more slowly when Nd^{3+} content increases.
Consequently it appears very interesting to substitute Ga for Al in LNA. However for laser application, the ability of the material to be elaborated in the form of good quality single crystals must be considered.

Crystal growth

Contrary to the LNA the melting of the pure gallate is not congruent . However, for the aluminogallates, crystal growth is possible. Single crystals of $(La_{1-x}Nd_x)_{1-z/3}Mg_{1-z}(Ga_{1-y}Al_y)_{11+z}O_{19}$ aluminogallates have been grown by Czochralski method under N_2 atmosphere containing 1 % O_2. The pulling and seed rotation rates were respectively 0.5 mm h^{-1} and 10 rpm. Due to the non congruency of the compounds the amount of Al and Mg in the crystals was higher than in the melt (Table 1).

Table 1 - Comparison of melts and crystals compositions (in mol. per cent) for several crystal growth experiments

Cristal number	Melt composition					Crystal composition				
	La_2O_3	Nd_2O_3	MgO	Ga_2O_3	Al_2O_3	La_2O_3	Nd_2O_3	MgO	Ga_2O_3	Al_2O_3
1	0.1480	0.0176	0.1086	0.4760	0.2494	0.0679	0.0036	0.1429	0.3536	0.4321
2	0.1720	0.0210	0.0980	0.4940	0.2150	0.0679	0.0036	0.1429	0.3214	0.4643
3	0.0692	0.0077	0.0769	0.5079	0.3383	0.0616	0.0030	0.0891	0.3133	0.5330
4	0.0697	0.0079	0.0770	0.5140	0.3314	0.0616	0.0030	0.0891	0.3727	0.4736

Quality of crystals decreases with the amount of Ga. Nevertheless, good platelets have been obtained with v > 0.55.
Fluorescence spectra for $^4F_{3/2} \rightarrow {}^4I_{11/2}$ Nd^{3+} transition have been recorded for several compositions (Fig. 3). They are similar to the LNA one (3).

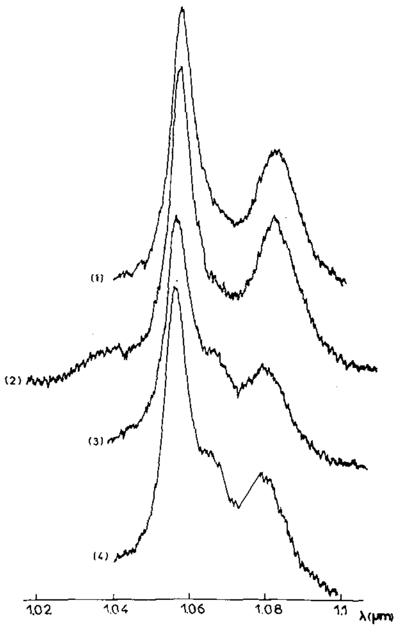

Figure 3
Nd^{3+} fluorescence spectra
($^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition)
for 4 aluminogallate single crystals
1 - $La_{0.95}Nd_{0.05}MgGa_{4.95}Al_{6.05}O_{19}$
2 - $La_{0.95}Nd_{0.05}MgGa_{4.5}Al_{6.5}O_{19}$
3 - $La_{0.83}Nd_{0.04}Mg_{0.6}Ga_{4.22}Al_{7.18}O_{19}$
4 - $La_{0.83}Nd_{0.04}Mg_{0.6}Ga_{5.02}Al_{6.38}O_{19}$

Conclusion

This work demonstrates that substitution of Ga for Al in LNA could improve the laser properties of this material : e.g. same power for smaller crystals, or increased power for crystals of the same size. Crystal growth of some other compositions of lanthanide aluminogallates and laser experiments are in progress in this laboratory.

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