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B. Martinat, A. Lejus, D. Vivien. ORIGIN OF THE INFRARED ABSORPTION IN LaMgAl₁₁O₁₉: Ti³⁺ A POTENTIAL LASER MATERIAL. Journal de Physique IV Proceedings, 1991, 01 (C7), pp.C7-343-C7-345. 10.1051/jp4:1991791 . jpa-00251034

HAL Id: jpa-00251034

<https://hal.science/jpa-00251034>

Submitted on 1 Jan 1991

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ORIGIN OF THE INFRARED ABSORPTION IN $\text{LaMgAl}_{11}\text{O}_{19}$: Ti^{3+} A POTENTIAL LASER MATERIAL

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Abstract - The $\text{LaMgAl}_{11}\text{O}_{19}$ matrix (magnetoplumbite structure) activated with Ti^{3+} could present broadly tunable laser action between 650 and 1000 nm. The optical absorption measurements show, in addition to the ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ transition of Ti^{3+} , two unexpected infrared bands. The first one, peaking at 730 nm, is attributed to an intervalence charge transfer transition of $\text{Ti}^{3+} - \text{Ti}^{4+}$ pairs located in (4f) sites. The second one, at 960 nm, is attributed to a $\text{Ti}^{2+} - \text{Ti}^{3+}$ charge transfer transition. These bands which occur in the range of the Ti^{3+} fluorescence wavelengths have to be suppressed for the lasing application of this material.

The $\text{LaMgAl}_{11}\text{O}_{19}$ hexaaluminate (LMA), with magnetoplumbite like structure, is well known as a remarkable good laser host. When the activator is Nd^{3+} , one obtains LMA:Nd or LNA, which has been widely studied (1)(2). This work deals with the activation of this matrix with Ti^{3+} ions which could present broadly tunable laser action between 650 and 1000 nm like Ti doped sapphire (3).

Single crystals of $\text{LaMgAl}_{11-x}\text{Ti}_x\text{O}_{19}$ are grown by flame fusion process (Verneuil method). In the matrix, Ti can be inserted in 3+ and 4+ oxidation state or in a mixture of both states. Traces of Ti^{2+} might be present. Previous ESR studies have demonstrated that Ti^{3+} is localized in the 3 octahedral sites (2a) (12k) (4f) of the structure with a strong preference for the (2a) site. Ti^{2+} would be situated in the (4f) site, the largest octahedral site (4). Compared to Ti: sapphire, there is no segregation of the doping ion and titanium solubility is much larger.

The optical absorption measurements (5) exhibit, in addition to an intense band peaking at 570 nm attributed to the ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ transition of Ti^{3+} , unexpected bands in the infrared. This is shown in figure 1 where the diffuse reflectance spectrum, performed on ground crystals, can be fitted as a sum of three Gaussian bands centered at 730, 960 and 1240 nm. We have only considered the two main bands at 730 and 960 nm with the aim to determine their origin and to try to suppress them. In fact, these bands occur in the range of the Ti^{3+} fluorescence wavelengths and they may have disastrous consequences for the laser application of this material.

From the behavior and the polarization of these bands, several hypotheses have been proposed (see Table I) (5)

Figure 1 : Diffuse reflectance spectrum of $\text{LaMgAl}_{10.99}\text{Ti}_{0.01}\text{O}_{19}$

Table I : Unwanted absorption bands

	730 nm	960 nm
Dichroïsm	strong	strong
$x \uparrow$	$\uparrow$	$\uparrow$
H ₂ treatment	$\downarrow 0$	$\rightarrow$
O ₂ treatment	$\downarrow 0$	$\downarrow 0$

- Ti^{2+} d-d transition. The absorption bands would be located at 910, 560 and 430 nm. It is not the case

- Intervalence charge transfer transitions : (IVCT).

The existence of $\text{Fe}^{2+}\text{-Ti}^{4+} \rightarrow \text{Fe}^{3+}\text{-Ti}^{3+}$ (as in sapphire (6)) has been proposed but can be discarded because no significant change in the absorption band intensities is observed by changing the Fe^{2+} or Ti^{4+} content.

The Ti-Ti IVCT transitions seem the most probable. In this case, the 760 nm band would be due to a $\text{Ti}^{3+} - \text{Ti}^{4+}$ IVCT. This is in agreement with the experimental observations. The 960 nm band might be associated with a $\text{Ti}^{2+} - \text{Ti}^{3+}$ IVCT. In both cases, the titanium ions of the pair are located in adjacent (4f) sites (face sharing octahedra).

The 730 nm band can be suppressed by a reducing treatment. However, bleaching of the 960 nm band requires to prevent the existence of Ti^{2+} . This could be done by a careful ajustement of oxidation-reduction treatments.

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