

## Optical Properties of $\text{LaMgAl}_{11}\text{O}_{19} : \text{Ti}^{3+}$ , a Potential Tunable Laser Material

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This paper reports optical absorption and fluorescence measurements on titanium-doped lanthanum hexaaluminate  $\text{LaMgAl}_{11}\text{O}_{19}$  (referred to LMA : Ti). In addition to the  ${}^2T_2 \rightarrow {}^2E$  transition of  $\text{Ti}^{3+}$ , the optical absorption spectrum exhibits two infrared absorption bands in the wavelength range of the  $\text{Ti}^{3+}$  fluorescence. The first one peaking at 730 nm is ascribed to an intervalence charge transfer transition of coupled  $\text{Ti}^{3+}-\text{Ti}^{4+}$  pairs. The second one peaking at 960 nm might be associated with a  $\text{Ti}^{2+}-\text{Ti}^{3+}$  intervalence charge transfer transition. In both cases the titanium ions of the pair are located in adjacent face-sharing octahedral (4f) sites. Various attempts to suppress these absorption bands are described. The LMA : Ti fluorescence spectra contain contributions from  $\text{Ti}^{3+}$  ions in different sites of the LMA matrix. © 1990 Academic Press, Inc.

### I. Introduction

In recent years, single crystalline vibronic laser materials were widely investigated (1). Tunable laser materials, activated by  $\text{Ti}^{3+}$  ions, present a considerable interest because of the simple electronic structure of  $\text{Ti}^{3+}$  and of the lack of excited state absorption, since higher energy states of  $\text{Ti}^{3+}$  (4s and charge transfer states) are located far above the levels of the  $d^1$  configuration. The  $\text{Ti}^{3+}$  fluorescence band gives the broadest laser tuning range known for a transition metal-activated laser ( $\cong 400$  nm in  $\alpha\text{Al}_2\text{O}_3$ ). Presently, the only commercial titanium-activated laser is titanium-doped sapphire  $\text{Al}_2\text{O}_3 : \text{Ti}^{3+}$  (2). The problem of  $\text{Al}_2\text{O}_3 : \text{Ti}^{3+}$  is the low solubility of titanium in  $\text{Al}_2\text{O}_3$  ( $\leq 3 \times 10^{-3} \text{ Ti}^{3+}/\text{Al}^{3+}$  at 1300°C) (3). In the past few years, a new potential tunable

laser, titanium-doped lanthanum-magnesium hexaaluminate  $\text{LaMgAl}_{11-x}\text{Ti}_x\text{O}_{19}$  (LMA : Ti) has been studied (4–7). A previous work also demonstrated that a large amount of Al (up to one atom by formula unit) can be replaced by Ti in LMA matrix (8). The solubility of Ti is thus significantly higher in LMA than in the  $\text{Al}_2\text{O}_3$  matrix. We also showed previously that Ti ions exist in both 3+ and 4+ oxidation states, and are distributed among the three kinds of octahedral sites of the LMA unit cell (4, 8). The structure of LMA is of the hexagonal magnetoplumbite (MP) type (space group  $P6_3/mmc$ ) (9) and consists of spinel blocks separated by mirror planes (9, 10). Figure 1 depicts the ideal unit cell. The Wyckoff positions of cations, their coordination, the site symmetry, and the geometry of the coordination polyhedra are gathered in Table I. The present paper deals with the optical properties of LMA : Ti. It has previously

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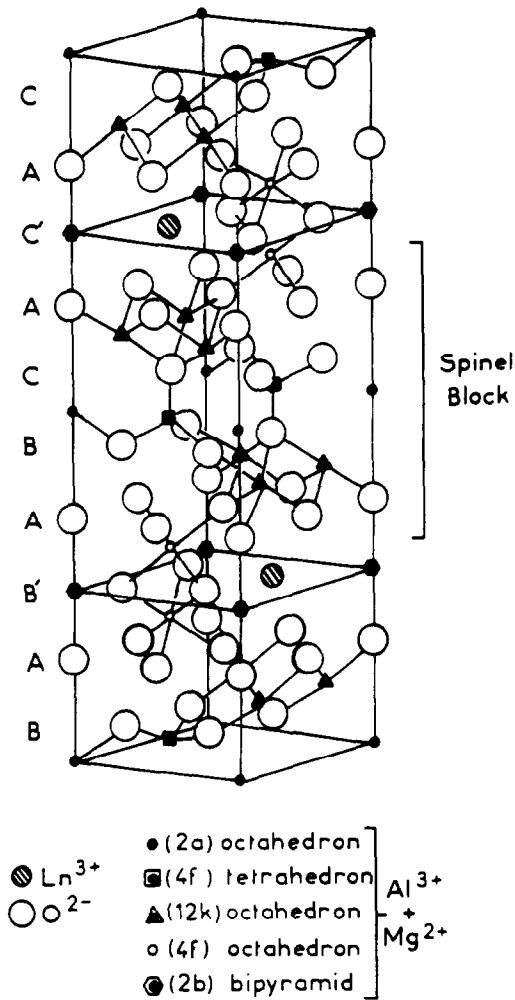


FIG. 1. Unit cell of  $\text{LaMgAl}_{11}\text{O}_{19}$  with magnetoplumbite structure, and identification of the various cationic sites.

TABLE I  
CATIONIC SITES IN LMA ( $\text{LaMgAl}_{11}\text{O}_{19}$ )

Site in Wyckoff notation	Atoms	Coordination	Geometry	Site symmetry
4f	$\text{Mg}^{2+}, \text{Al}^{3+}$	4	Tetrahedron	$C_{3v}$
4f	$\text{Al}^{3+}$	6	Distorted octahedron	$C_{3v}$
12k	$\text{Al}^{3+}$	6	Distorted octahedron	$C_s$
2a	$\text{Al}^{3+}$	6	Regular octahedron	$D_{3d}$
2b	$\text{Al}^{3+}$	5 (ideal)	Trigonal bipyramid	$D_{3h}$
(4e)		4 (real)	Tetrahedron	$C_{3v}$
2d and (6h)	$\text{La}^{3+}$	12 and (8)	Dodecahedron	$D_{3h}$ and $(C_{2v})$

been shown that the optical absorption spectra of LMA : Ti crystals at room temperature present two bands around 730 and 960 nm in addition to the  $d-d$  band of  $\text{Ti}^{3+}$  around 550 nm (5). The near infrared bands are strongly dichroic and appear only when the electric field  $\mathbf{E}$  of the incident light is parallel to the  $c$  axis (5). These bands are annoying because they occur in the same wavelength range as the  $\text{Ti}^{3+}$  fluorescence in LMA, and impede laser applications of this material (11). The aim of this study is first to investigate the nature of these two optical absorption bands and to try to suppress them. Also, it is known that the distribution of  $\text{Ti}^{3+}$  ions among the different octahedral sites of the LMA lattice depends upon the titanium doping level of the material (8). Therefore, another purpose of this work was to determine the influence of the titanium content on the fluorescence spectrum of LMA : Ti.

## II. Experimental

Single crystals with starting compositions  $\text{LaMgAl}_{11-x}\text{Ti}_x\text{O}_{19}$  ( $0.011 \leq x \leq 1.65$ ) were obtained by the Verneuil process, using a strongly reducing flame ( $\text{H}_2/\text{O}_2$  flow  $> 3$ ), according to the method described previously (8). Crystals grow along the  $a$  crystallographic axis of the MP unit cell. Under mechanical shock, they cleave, giving single crystalline platelets perpendicular to the  $c$  axis.

A few crystals ( $x = 0.022$  and  $x = 0.055$ ) were grown by the "inverted torch" Verneuil process that gives more oxidizing conditions ( $\text{O}_2/\text{H}_2$  flow greater than 1.5). They contain titanium almost entirely at the  $4+$  oxidation state (8).

Powder samples corresponding to  $x = 0.022$  and  $x = 0.055$  were prepared by coprecipitation of the amorphous hydroxides followed by annealing at  $1200^\circ\text{C}$  for 3 days under  $\text{H}_2$  atmosphere (8). Other samples were also melted in an argon-hydrogen plasma torch ( $\text{H}_2/\text{Ar} = 0.05$ ). These

strongly reducing treatments imply that these compounds are almost completely free of  $\text{Ti}^{4+}$  ions.

The optical absorption spectra were recorded using a Kontron UV 860 spectrometer. The  $c$  axis of small single crystalline platelets is parallel to the light beam direction. However, the observation of the two IR absorption bands requires that the light propagates perpendicular to  $c$ , which cannot be achieved with the available cleavage platelets. For this reason and also because some samples were prepared in the powdered form, we use diffuse reflectance instead of absorption spectra. These spectra were recorded at room temperature using a Beckman 5270 spectrometer fitted with an integrating sphere. The reference powder was  $\text{BaSO}_4$  and the spectral range 700–1500 nm.

The fluorescence spectra were recorded on a Raman spectrometer HG2S from Jobin-Yvon; LMA:Ti crystals were excited by the 5145 Å line of an argon ion laser.

### III. Results

A typical optical absorption spectrum of a LMA:Ti ( $x = 0.022$ ) single crystal is given in Fig. 2. It exhibits an intense UV absorption and an absorption band peaking

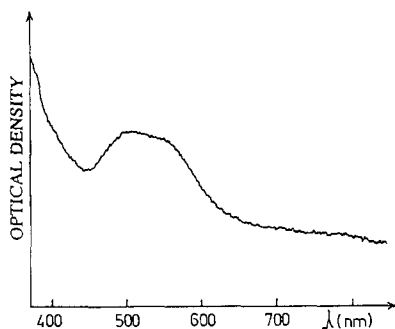


FIG. 2. Optical absorption spectrum at room temperature of a LMA:Ti ( $x = 0.022$ ) single crystal annealed under pure hydrogen atmosphere ( $T = 1200^\circ\text{C}$ , 72 hr).

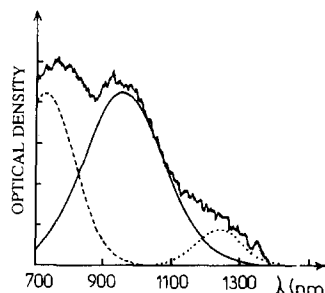


FIG. 3. Diffuse reflectance spectrum of LMA:Ti ( $x = 0.011$ ) crystal annealed under pure hydrogen atmosphere ( $T = 1200^\circ\text{C}$ , 72 hr).

at 570 nm. This band, with a shoulder at 520 nm, is attributed to the  ${}^2T_2 \rightarrow {}^2E$  transition characteristic of  $\text{Ti}^{3+}$  in an octahedral crystal field as in  $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$  (12). The splitting of the band could arise from the multisite character of  $\text{Ti}^{3+}$  in LMA (4), or from a Jahn–Teller splitting of the  ${}^2E$  excited state, as observed usually with  $\text{Ti}^{3+}$ -activated materials (12).

A typical diffuse reflectance spectrum of a powder obtained by grinding a LMA crystal ( $x = 0.011$ ) which has been annealed under  $\text{H}_2$  is given in Fig. 3. This spectrum can be fitted as a sum of three Gaussian bands centered respectively at 730, 960, and 1240 nm. The weak band at 1240 nm will not be further considered because of lack of information on its polarization and its behavior in various crystal treatments. However, weak absorptions in this region have recently been observed in single crystals with  $\sigma$  polarized light (11).

The behavior of the two main absorption bands under various treatments is summarized in Table II for different samples and is described below.

We shall first consider crystals elaborated by the classical Verneuil process (reducing atmosphere). In these crystals, the 730- and 960-nm band intensities increase with the titanium content  $x$ . Under oxidizing treatment (3 days in air at  $1360^\circ\text{C}$ ), the two infrared bands and the  $d-d$   $\text{Ti}^{3+}$  band disappear.

TABLE II

EVOLUTION OF THE INFRARED ABSORPTION BAND INTENSITIES OF LMA:Ti ACCORDING TO THE SYNTHESIS AND ANNEALING CONDITIONS OF THE MATERIAL;  $x$  IS THE STARTING Ti/(Al + Ti) ATOMIC RATIO

	730-nm band	960-nm band
Normal Verneuil process (reducing atmosphere)		
Increasing titanium content $x$	↓	→
Annealing the as-grown crystals at 1200°C under H <sub>2</sub> atmosphere	↓	↓
Annealing at 1360°C in air	↓	↓
"Inverted torch" Verneuil process (oxidizing atmosphere)		
Increasing titanium content $x$	↑	↑
Annealing the as-grown crystals at 1200°C under H <sub>2</sub> atmosphere	↑	↑
For 17 hr	↑	↑
For 72 hr	↑	↑
Annealing at 1360°C in air	↓	↓
Annealing of coprecipitates at 1200°C under H <sub>2</sub> atmosphere	Missing	Strong
Melting in a (Ar + 5% H <sub>2</sub> ) plasma torch	Missing	Strong

After a reducing treatment (3 days at 1200°C under hydrogen atmosphere), the intensity of the 730-nm band decreases. On the contrary, the intensity of the 960-nm one increases for low, and decreases for high titanium contents. A prolonged reducing treatment completely bleaches the 730-nm band but not the 960-nm one.

In the case of crystals elaborated by the "inverted torch" Verneuil process (oxidizing atmosphere), the two absorption bands are observed and their intensities also increase with the titanium content. The band intensities increase after a reducing treatment (3 days at 1200°C under hydrogen atmosphere). A longer reducing treatment leads to the disappearance of the 730-nm band but not of the 960-nm one. After an oxidizing treatment (3 days in air at 1360°C), the two bands disappear.

The results for coprecipitates annealed at 1200°C under hydrogen atmosphere and samples elaborated by melting in the (Ar + 5% H<sub>2</sub>) plasma torch are different since

the diffuse reflectance spectra of these samples present only an intense absorption band at 960 nm.

The fluorescence spectra of all our crystals exhibit a wide band extending from 650 to beyond 850 nm (the cutoff of the spectrometer PMT). A narrow peak at 1445 cm<sup>-1</sup> originating from Cr<sup>3+</sup> impurities is often observed (13). Both the intensity and the shape of the fluorescence band are dependent upon the titanium content  $x$  and reducing treatments. We have investigated two crystals corresponding to  $x = 0.022$  and  $x = 0.055$ , before and after annealing at 1200°C for 72 hr under hydrogen atmosphere. Figure 4 shows the fluorescence spectra of LMA:Ti for the crystal with  $x = 0.055$ . It can be seen that the fluorescence bands of Ti<sup>3+</sup> in the LMA matrix is shifted toward longer wavelengths after annealing. The same behavior occurs for the crystal corresponding to  $x = 0.022$ . The fluorescence intensity increases for reduced crystals because the reducing treatment converts all the Ti<sup>4+</sup> into Ti<sup>3+</sup> while the as-grown crystals contain only 33% of titanium at the 3+ state (8).

Four crystals corresponding to starting titanium contents of  $x = 0.022, 0.055, 0.11,$  and  $0.22$  were annealed at 1200°C for 72 hr under hydrogen atmosphere. Figure 5 shows the fluorescence spectra of the re-

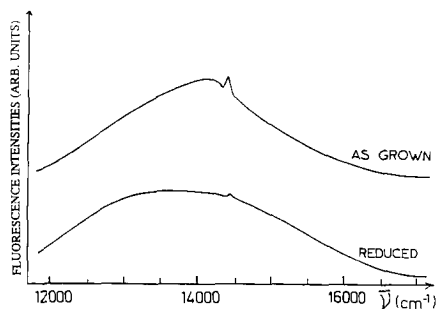


FIG. 4. Fluorescence spectra of Ti<sup>3+</sup> in LMA:Ti crystal ( $x = 0.055$ ). The excitation wavelength is  $\lambda = 5145 \text{ \AA}$ .

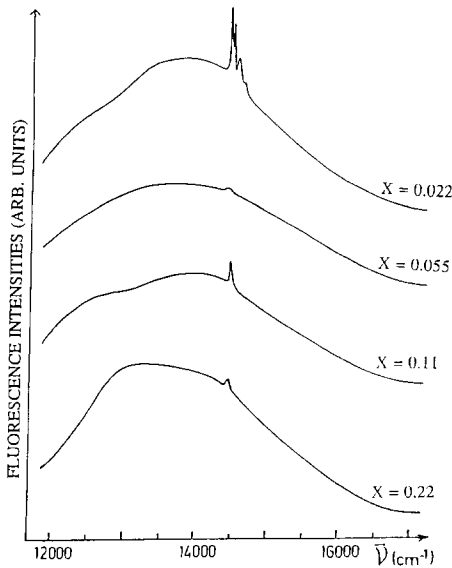


FIG. 5. Fluorescence spectra of  $\text{Ti}^{3+}$  in  $\text{LMA}:\text{Ti}$  crystals. The excitation wavelength is  $\lambda = 5145 \text{ \AA}$ . The samples were reduced under pure hydrogen atmosphere ( $T = 1200^\circ\text{C}$ , 72 hr).

duced crystals. It can be seen that the  $\text{Ti}^{3+}$  fluorescence band is shifted toward longer wavelengths, and the fluorescence intensity decreases when  $x$  increases. The crystal corresponding to  $x = 0.022$  presents the strongest intensity.

We failed to obtain selective excitation of  $\text{Ti}^{3+}$  fluorescence on a reduced crystal ( $x = 0.22$ ), using the various wavelengths of the Argon ion laser: 4764, 4879, 4965, 5017, and 5145  $\text{\AA}$ . All the fluorescence spectra obtained under these various excitation lines are identical.

#### IV. Discussion

We shall now focus on the origin of the infrared absorption bands. These bands do not exist in the pure LMA matrix. They appear only when Ti is incorporated in the matrix and evolve along with titanium content  $x$ . These bands are thus associated with the presence of titanium, but in a reduced

oxidation state. Indeed, they vanish under oxidizing and reappear under reducing treatments. These bands cannot be due to  $\text{Ti}^{3+}$  ion, because this gives only one broad  $d-d$  band at  $\sim 570 \text{ nm}$ . In a previous study dealing with the EPR of  $\text{Ti}^{3+}$  in the LMA matrix (8), we postulated the existence of  $\text{Ti}^{2+}$  in the ( $4f$ ) octahedral site. It remains questionable if these infrared bands can be assigned to  $\text{Ti}^{2+}$   $d-d$  transitions. To our knowledge, the  $Dq$  and  $B$  values for  $\text{Ti}^{2+}$  in octahedral environment in oxides are unknown. However, for  $\text{Ti}^{2+}$  in octahedral chlorine environment (in  $\text{MgCl}_2$ ) the literature gives  $Dq = 1018 \text{ cm}^{-1}$  and  $B = 527 \text{ cm}^{-1}$  (14). A reasonable estimation for the crystal field and Racah parameters can be deduced for the ( $\text{Ti}^{2+}\text{O}_6$ ) chromophore, from the evolution of  $Dq$  and  $B$  for other octahedral divalent transition metal ions (such as  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ), which have been studied both in oxide and in chlorine ion environments (15). We propose  $Dq = 1200 \text{ cm}^{-1}$  and  $B = 530 \text{ cm}^{-1}$ . With these parameters,  $\text{Ti}^{2+}$  ( $d^2$  ion) should give rise to three spin allowed absorption bands located at 910, 560, and 430 nm (16). This does not fit with either the 730- or the 960-nm band under study. On the contrary, if we change the  $Dq$  parameter to fit the 960-nm band ( $Dq = 1140 \text{ cm}^{-1}$ ) the two other bands are expected at 575 and 460 nm, but there is no absorption at 460 nm in the experimental spectrum (Fig. 2). We thus assume that the transitions responsible for the infrared absorption bands of  $\text{LMA}:\text{Ti}$  cannot arise from simple ions. However, they may originate from an optical intervalence charge transfer transition (IVCT) since these bands occur in a wavelength range where IVCT have already been observed in other materials (17–19). Such transitions are spin and symmetry allowed. Typically, oscillator strengths of a  $d-d$  transition and of a charge transfer transition are of the order of  $10^{-4}$  and  $10^{-1}$ , respectively (20), so that the pair concentration in  $\text{LMA}:\text{Ti}$  could be very low (of the order

of few ppm) and nevertheless give a strong absorption band.

The problem is now to determine the nature of the ions constituting the pair. Iron ions always occur as impurity in LMA crystals (21), so that an IVCT transition between coupled iron–titanium ion pairs, i.e.,  $\text{Fe}^{2+}-\text{Ti}^{4+} \rightarrow \text{Fe}^{3+}-\text{Ti}^{3+}$ , as in sapphire (12), could be responsible for the infrared bands. To check this hypothesis, we prepared several samples with various iron and titanium contents. In order to change the  $\text{Fe}^{2+}$  content, we prepared two kinds of LMA : Ti crystals:

(i) crystals doped with  $\text{Fe}^{2+}$ , in order to increase their Fe content and therefore the number of Fe–Ti pairs;

(ii) crystals with excess  $\text{Mg}^{2+}$ . Since  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  ions share the same sites (22), increasing the  $\text{Mg}^{2+}$  content implies a decrease of the amount of  $\text{Fe}^{2+}$  ions and consequently of the number of Fe–Ti pairs. In both cases, there is no significant evolution of the infrared absorption band intensities.

Concerning the  $\text{Ti}^{4+}$  content, we prepared crystals of LMA : Ti but with  $\text{Hf}^{4+}$  or  $\text{Zr}^{4+}$  ions added, which are supposed to retain the (4+) oxidation state, constraining Ti to convert into the (3+) state in the matrix. This should also involve a decrease in the number of  $\text{Ti}^{4+}-\text{Fe}^{2+}$  pairs. In both cases, we observed no significant changes in the infrared absorption band intensities. Therefore assignment of one or both of these bands to  $\text{Fe}^{2+}-\text{Ti}^{4+}$  intervalence charge transfer transitions must be discarded. Alternatively, we postulate the existence of  $\text{Ti}^{3+}-\text{Ti}^{4+}$  and  $\text{Ti}^{2+}-\text{Ti}^{3+}$  IVCT, respectively, to explain the evolutions with  $x$  value and reducing/oxidizing treatment of the 730- and 960-nm bands (Table II). Under oxidizing treatment, the two bands disappear, titanium being only in its oxidized form ( $\text{Ti}^{4+}$ ). A prolonged reducing treatment completely bleaches the 730-nm band but not the 960-nm band. In this case titanium is in its reduced forms ( $\text{Ti}^{2+}$  or  $\text{Ti}^{3+}$ ).

The infrared absorption bands of

LMA : Ti crystals exhibit a strong dichroism (5), which can be used to determine the localization of the ion pairs. We have then looked for the possible cationic pairs which could occur in the LMA matrix, by classifying them with respect to the principal crystal axis ( $c$  axis).

—The strong dichroism allows the elimination of pairs whose axes are not either parallel or perpendicular to  $c$  (the case of the (2a)–(12k) pair). Intervalence transition of such a pair should be observed both for  $\mathbf{E} \parallel c$  and  $\mathbf{E} \perp c$ .

—The (12k)–(12k) pair is strictly perpendicular to the  $c$  axis, and the (2a)–( $4f_{\text{etra}}$ ), ( $4f_{\text{oct}}$ )–(2b) pairs are close to the  $c$  direction. If the pair is perpendicular to  $c$ , the  $z$  axis is along the pair axis. To observe a strong dichroism in this case,  $x$  and  $y$  must belong to different irreducible representations of the pair symmetry group. This is possible only for the point groups  $C_{2v}$ ,  $D_2$  and  $D_{2h}$ . However, these symmetries do not correspond to the above-mentioned pairs, which have lower symmetries ( $C_s$  or  $C_i$ ). In that case,  $x$  and  $y$  belong to the same representation.

—The (2a)–(2b) and ( $4f_{\text{oct}}$ )–( $4f_{\text{oct}}$ ) pairs are strictly parallel to the  $c$  axis. Since there are no oxygen ions shared between the (2a) and (2b) sites, interaction between two ions in these sites is expected to be very weak. We are thus left only with the ( $4f_{\text{oct}}$ )–( $4f_{\text{oct}}$ ) pairs. The two (4f) octahedra are face-sharing and the distance between the two metal ions is only 2.66 Å. This distance is very short and a strong cation–cation interaction is expected to occur in that case.

Such interactions are necessary for the occurrence of IVCT (23, 24). The symmetry of this pair of trigonally distorted sites is  $C_{3v}$ . Since the two IVCT transitions involve only titanium ions, which differ by their oxidation states, the ground and excited states of the IVCT should have exactly the same symmetry because they are related through permutation of the atoms of the pair. In  $C_{3v}$

symmetry, ions pairs may have only three different states of  $A_1$ ,  $A_2$  and  $E$  types. The three possible optically induced IVCT are thus  $A_1 \rightarrow A_1$ ,  $A_2 \rightarrow A_2$  and  $E \rightarrow E$ . The two  $A \rightarrow A$  transitions are electric-dipole allowed for  $\mathbf{E} \parallel \mathbf{c}$  and forbidden for  $\mathbf{E} \perp \mathbf{c}$ , while the  $E \rightarrow E$  transition is allowed for all the electric field orientations.

Let us first consider the 730-nm band, which was assigned to a  $\text{Ti}^{3+}-\text{Ti}^{4+}$  IVCT. It was previously demonstrated (4) that the  $\text{Ti}^{3+}$  ground state in a ( $4f_{\text{oct}}$ ) site is  ${}^2A_1$ ,  $\text{Ti}^{4+}$  being a closed shell ion, the ground state of the pair is also  ${}^2A_1$ , and the IVCT should be a  ${}^2A_1 \rightarrow {}^2A_1$  transition, which is allowed only for  $\mathbf{E} \parallel \mathbf{c}$  as found experimentally.

The situation is more complicated for the 960-nm band, attributed to a  $\text{Ti}^{2+}-\text{Ti}^{3+}$  pair. The IVCT should have the same polarization as the  $\text{Ti}^{3+}-\text{Ti}^{4+}$  IVCT only if the ground and excited states of the pair are  $A_1$  or  $A_2$ . Thus, detailed calculation should be performed on this pair to confirm our model for the 960-nm band.

The interpretation of the fluorescence spectra is straightforward. Previous studies of  $\text{LMA}:\text{Ti}$  (4), concerning crystals weakly doped, showed that  $\text{Ti}^{3+}$  ions are distributed among the three kinds of octahedral sites of the MP unit cell, the (2a) site being the most populated. When the  $x$  content increases, this site always remains the most populated, but the  $\text{Ti}^{3+}$  content of the ( $4f_{\text{oct}}$ ) site increases markedly and becomes close to that of (2a) for  $x = 1.65$  (limit of existence of  $\text{LMA}:\text{Ti}$  single crystals). On the contrary, the distribution of  $\text{Ti}^{3+}$  in the (12k) site is approximately constant to about 13% (8). We have demonstrated that the fluorescence band of  $\text{Ti}^{3+}$  in the  $\text{LMA}$  matrix is shifted toward higher wavelengths, when the  $\text{Ti}^{3+}$  content increases either by reductive annealing or by increasing  $x$  in the as-grown crystals. This can be explained by the fact that titanium ions located in different sites, ( $4f_{\text{oct}}$ ) and (12k) of the  $\text{LMA}$  matrix, contribute to the fluorescence emission.

## V. Conclusion

The absorption spectra of  $\text{LMA}:\text{Ti}$  exhibit two main absorption bands due to intervalence charge transfer transitions. From the polarization of these bands, it is deduced that the two metal ions involved in these charge transfers are located in two adjacent ( $4f_{\text{oct}}$ ) sites. The 730-nm band, which is attributed to  $\text{Ti}^{3+}-\text{Ti}^{4+}$  charge transfer, can be suppressed by reductive treatments. The 960-nm band is tentatively attributed to a  $\text{Ti}^{2+}-\text{Ti}^{3+}$  charge transfer transition. The next step in these investigations will be to prevent the existence of Ti in the (2+) oxidation state by the adjustment of oxidation–reduction treatments.

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