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OPTICAL CHARACTERIZATION OF Nd³⁺ DOPED CaF₂ LAYERS GROWN BY MOLECULAR BEAM EPITAXYL.E. BAUSA^{*,(1)}, R. LEGROS^{*} and A. MUNOZ-YAGUE^{*}*^{*}Laboratoire d'Automatique et d'Analyse des Systèmes du CNRS, 7 avenue du Colonel Roche, F-31077 Toulouse Cedex, France*

Abstract - Nd³⁺ doped CaF₂ monocrystalline films have been grown by molecular beam epitaxy using CaF₂ and NdF₃ evaporation on CaF₂ substrates. The effect of Nd³⁺ concentration is studied by means of the photoluminescence signal of Nd³⁺ ions. The results can be compared favourably with those obtained on CaF₂:Nd bulk crystals. For a given Nd³⁺ concentration a lower quantity of Nd³⁺ aggregate centers is observed. Nd³⁺ ions can therefore be efficiently incorporated as isolated Nd³⁺-F-centers up to a concentration of 6 wt % Nd³⁺ without emission quenching of their associated line at 1045.7 nm.

1 - Introduction

Nd³⁺ ions are the most widely used activators in solid-state laser and stimulated emission has been observed for numerous neodymium-doped crystals, including a great number of fluoride matrices [1]. The main transition used for laser emission at room temperature takes place between ⁴F_{3/2} and ⁴I_{11/2} multiplets of Nd³⁺. On the other hand, some absorption lines belonging to the transition between the ⁴I_{9/2} and ⁴F_{3/2} levels overlap the emission lines of GaAs-GaAlAs semiconductor lasers. Thus, laser action from diode laser pumped Nd³⁺ activated crystals have been demonstrated. In this sense, association of a semiconductor diode laser with a thin film Nd-doped crystal could lead to promising optoelectronic devices.

Monocrystalline thin film of CaF₂ has been selected as a matrix for Nd³⁺ ions. Indeed laser action has been demonstrated for CaF₂:Nd bulk crystals [2] and CaF₂ can be epitaxially grown on semiconductor substrates [3]. In the work we present here, the epitaxial growth was carried out on CaF₂ bulk crystals.

2 - Experimental

Monocrystalline thin layers of Nd-doped CaF₂ were grown on (100) and (111) CaF₂ substrates by molecular beam epitaxy (MBE). The substrates were mechanochemically polished, mounted on molybdenum blocks and loaded in a ultra-high vacuum chamber. The temperature of the two evaporation cells loaded with CaF₂ and NdF₃ was used to control the growth rate (0.1 to 1 μm/h) and the impurity concentration, respectively. As demonstrated in a previous paper [4], the sticking coefficient of Nd is very close to unity. Here, we report on samples containing between 0.3 and 10 wt % Nd³⁺. A good crystallinity was obtained at a substrate temperature of 500°C, as observed by reflection high energy electron diffraction analysis during growth.

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The luminescence measurements were performed at 77K. The luminescence was excited by the 514.5 nm line of an Ar⁺ laser (P=80 mW) and analysed by a 1m Jobin-Yvon grating spectrometer followed by a GaAs cathode photomultiplier (up to 930 nm) or a cooled Ge photodiode for the range 1 μ m-1.1 μ m. The presented spectra were not corrected for the response of the photodetectors.

3 - Results and discussion

Figure 1 shows a characteristic photoluminescence spectrum obtained on a sample with low doping concentration (0.3 wt %) for the two spectral regions we have studied. The first one, from 850 to 930 nm, corresponds to the Nd³⁺ emission lines from $^4F_{3/2} \rightarrow ^4I_{9/2}$ transitions of this ion ; the second, from 1040 to 1100 nm corresponds to the lines associated with the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition.

Before examining the features of this spectrum, we have to recall some results concerning the incorporation of Nd³⁺ in the CaF₂ matrix.

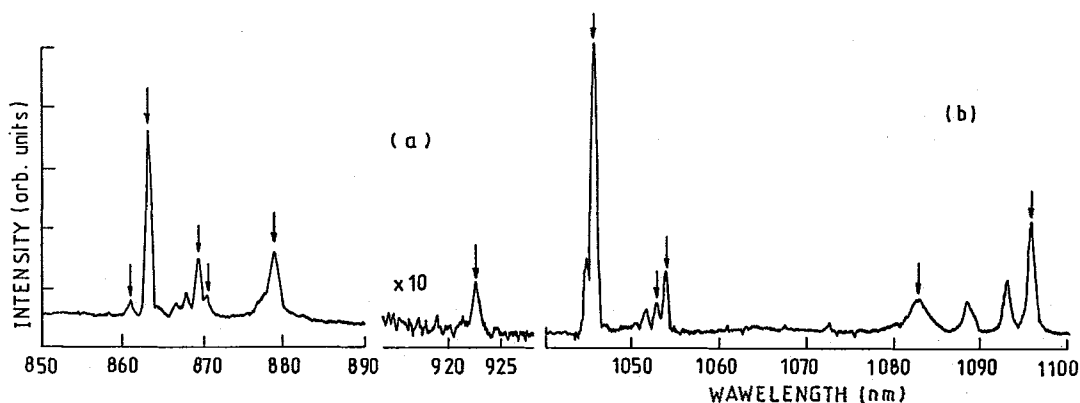


Figure 1: Luminescence spectra for a 0.3 wt % Nd³⁺ doped CaF₂ layer : (a) emission lines corresponding to $^4F_{3/2} \rightarrow ^4I_{9/2}$ Nd³⁺ transitions ; (b) idem for $^4F_{3/2} \rightarrow ^4I_{11/2}$ Nd³⁺ transitions. Arrows show the emissions from L centers.

It is well known that a charge compensation mechanism is required when a rare earth trivalent ion substitutes for a divalent ion in a fluoride matrix. In our samples, the use of NdF₃ as a source for Nd³⁺ provides the excess of F⁻ ions in interstitial position to ensure the afore mentioned charge compensation mechanism. As in bulk crystals, this produces Nd³⁺-F⁻ dipoles in the <100> direction, in which Nd³⁺ ions are in C_{4v} symmetry sites [5]. Because of their large binding energy, Nd³⁺ and F⁻ are associated in pairs or more complex structures [6]. Optical spectroscopy and electron paramagnetic resonance investigations have also shown that, for concentrations around 1 wt % Nd³⁺, three types of Nd centers exist : the L or tetragonal center (Nd³⁺-F⁻) and two orthorhombic centers, M and N, which are formed by the association of two and four L centers respectively [7][8].

The whole spectrum presented on figure 1 is in agreement with those already published for CaF₂:Nd bulk crystals with very diluted Nd concentrations [9].

The lines associated with transitions between levels of tetragonal centers are identified by an arrow. The others lines must be associated with more complex centers of orthorhombic symmetry. Due to the low concentration of Nd, the later are weak. It must be pointed out that the spectra obtained from bulk samples with similar Nd concentration, show M and N emission lines much more pronounced than our epitaxial layers.

Hereafter we will focus our attention on the line at 1045.7 nm (L line) because this transition is widely used when stimulated emission is investigated. The influence of Nd concentration on the relative intensity of L and N lines and on the absolute intensity of the emissions will be detailed.

On figure 2 three photoluminescence spectra in the $4F_{3/2} \rightarrow 4I_{11/2}$ emission region obtained on samples containing 0.3 to 3.7 wt % Nd are presented.

In this spectral region (1.04-1.06 μm), the lines associated with L, M and N centers were previously well characterized in bulk crystals [9]. In accordance with these results, we clearly observe the lines associated with the three types of centers (see labels in the figure). It can be noted that the relative intensity of the three emission lines changes to the benefit of the L line when the Nd content is decreased.

When comparing our results to published data on bulk crystals [7,9], it can be observed that the concentration of L centers relative to aggregate centers appears to be higher in the MBE grown layers : concerning the M-type centers, the comparison is very advantageous to epitaxial layers; the ratio between L centers to M centers emission intensities is equal to 4 for a 1 wt % Nd doped CaF_2 crystal, whereas in our case that ratio is much higher, and this appears to be the case even for concentrations as high as 10 wt % Nd.

According to the above considerations, the ratio between the emission intensities corresponding to L centers and N centers measures in our samples the aggregation state of the Nd^{3+} . Figure 3 gives this ratio as a function of Nd content in the samples under study.

Figure 4 illustrates the influence of Nd concentration on the emission intensity of the 1045.7 nm peak (L line). Up to 6 wt %, the intensity increases linearly. The results previously obtained for Nd^{3+} ions in CaF_2 bulk crystals show that luminescence quenching is effective beyond 0.1 wt % Nd^{3+} . This final result demonstrates the superior performance of epitaxial material in comparison with bulk crystals. The low concentration of M and N aggregates allows incorporation of Nd at high concentration without significant quenching of the 1045.7 nm emission.

This tendency of Nd ions to form mainly tetragonal centers could be explained by the growth temperature. Epitaxial growth takes place at much lower temperatures than those used for bulk crystal growth. This greatly influences the formation of aggregates which depends on total Nd concentration and on temperature which governs solid state diffusion ; indeed, it has

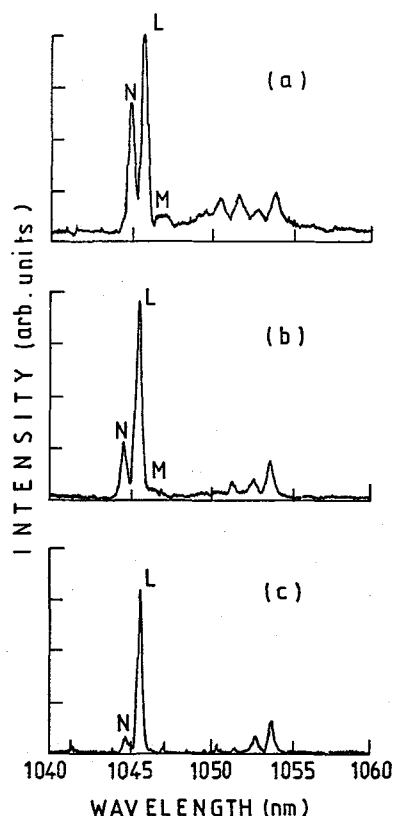


Figure 2: Nd^{3+} luminescence spectra in the $4F_{3/2} \rightarrow 4I_{11/2}$ region for layers with different Nd^{3+} content : (a) 3.7 wt% ; (b) 1.1 wt% and (c) 0.3 wt%.

been reported that complexes $\text{Nd}^{3+}\text{-F}^-$ become virtually immobile at temperatures less than 600°C [6].

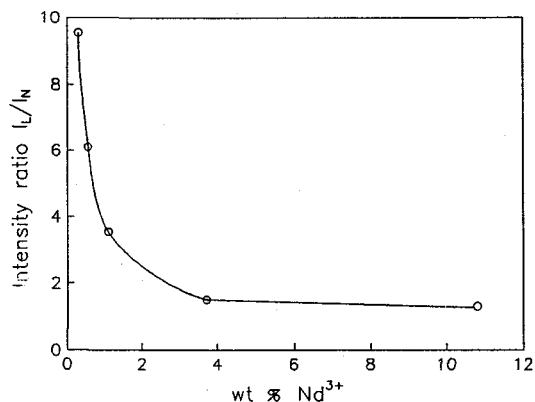


Figure 3: Intensity ratio I_L/I_N calculated for the luminescence lines at 1045.7 and the 1045.7 nm emission line.

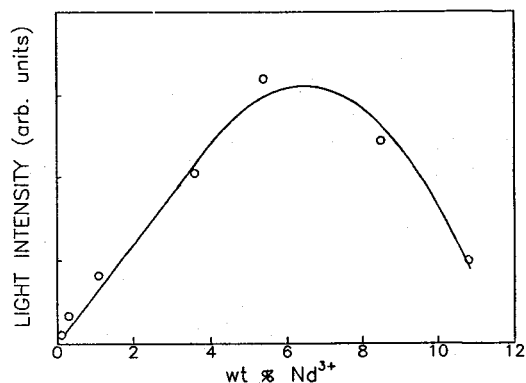


Figure 4: Emission intensity at 77 K as a function of Nd^{3+} concentration for 1044.8 nm.

A last question is the role that crystal orientation plays in the processes of NdF_3 dissociation when incorporating in the CaF_2 matrix and in aggregate formation.

The I_L/I_N relationship is identical for two samples grown simultaneously on (100) and (111) CaF_2 oriented substrates. This can be observed from the spectra shown in figure 5(a) and 5(b) corresponding to epitaxial layers grown on CaF_2 substrates with (100) and (111) orientation respectively. This result allows to deduce that Nd^{3+} aggregation is not dependent on the orientation of the growing surface and, hence, only bulk mechanisms related to growth temperature have an influence on the formation of Nd complex centers in the epitaxially grown $\text{CaF}_2\text{:Nd}$ layers.

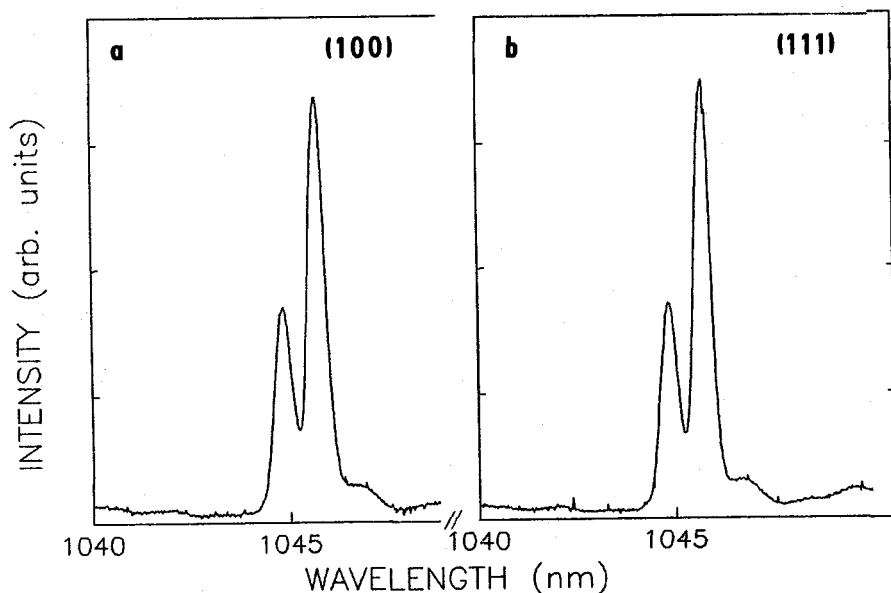


Figure 5: Photoluminescence spectra of Nd^{3+} in CaF_2 layers grown on oriented monocrystalline substrate of CaF_2 . Orientation : (a) (100) and (b) (111).

4 - Conclusion

Monocrystalline thin layers of Nd-doped CaF_2 on (100) CaF_2 substrates have been epitaxially grown by MBE. Close control of the doping level was obtained by varying the flux of NdF_3 .

We have used photoluminescence measurements to study the incorporation of Nd in CaF_2 . Due to the charge compensation mechanism most of the Nd^{3+} ions forms isolated complex centers ($\text{Nd}^{3+}\text{-F}^-$). The concentration of M- and N-type aggregates is lower than that observed for moderate Nd^{3+} concentration (around 1 wt %) in bulk CaF_2 crystals.

The thermodynamical conditions during MBE growth (namely the low growth temperature) explain the high efficiency of Nd incorporation and the inability of Nd^{3+} to diffuse and to form more complex centers.

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