0.85 and 1.54 μm emissions of $\text{CaF}_2\text{:Er}^{3+}$ layers grown by molecular beam epitaxy

E. Daran, R. Legros, A. Muños-Yagüe, C. Fontaine, L. Bausá

► To cite this version:

E. Daran, R. Legros, A. Muños-Yagüe, C. Fontaine, L. Bausá. 0.85 and 1.54 μm emissions of $\text{CaF}_2\text{:Er}^{3+}$ layers grown by molecular beam epitaxy. Journal de Physique IV Proceedings, 1994, 04 (C4), pp.C4-397-C4-401. 10.1051/jp4:1994495 . jpa-00252758

HAL Id: jpa-00252758

<https://hal.science/jpa-00252758>

Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

0.85 and 1.54 μm emissions of $\text{CaF}_2\text{:Er}^{3+}$ layers grown by molecular beam epitaxy

E. DARAN, R. LEGROS, A. MUÑOS-YAGÜE, C. FONTAINE and L.E. BAUSÁ*

Laboratoire d'Automatique et d'Analyse des Systèmes du CNRS, 7 Av. Colonel Roche, 31077 Toulouse cedex, France

** Departamento de Física de Materiales C-IV, Universidad Autonoma de Madrid Cantoblanco, 28049 Madrid, Spain*

ABSTRACT

Molecular beam epitaxy of CaF_2 monocrystalline layers Er^{3+} doped up to a concentration of 50 mol% is demonstrated on CaF_2 substrates. Separated effusion cells containing CaF_2 and ErF_3 have been used. The photoluminescence spectra of these thin layers exhibit emissions from centers which were found to correspond to those already reported for $\text{CaF}_2\text{:Er}^{3+}$ bulk crystals. The influence of growth temperature and Er concentration on the spectroscopic properties of these layers was investigated. The 1.54 μm emission of interest was shown to behave as aggregate centers, and the integrated luminescence was only quenched for concentrations higher than 35 mol%. The trends observed evidence that molecular beam epitaxy is a powerful technique for growing thin Er-doped fluoride layers.

1. Introduction :

Crystals activated by rare-earth ions are among the most extensively studied solid-state lasers that can be pumped by semiconductor laser diodes. Specially, much effort has been focussed on these materials as thin films, as this will allow solid-state device integration.

In this paper, we investigate the optical properties of $\text{CaF}_2\text{:Er}^{3+}$ thin layers grown by molecular beam epitaxy on CaF_2 substrates. Er^{3+} produces an emission at a wavelength of 1.54 μm , which is of great interest for telecommunication systems. The influence of growth parameters and Er concentration on the luminescence properties was investigated around 0.85 and 1.55 μm .

2. Experimental :

The (100) oriented CaF_2 substrates were degreased prior to being soldered with indium on a molybdenum block. Once under vacuum, they were heated up to a temperature of 550C to obtain an oxygen-free surface. CaF_2 and ErF_3 were then evaporated from separated effusion cells equipped with boron nitride crucibles. The use of ErF_3 as a source for Er^{3+} ions provided an excess of F^- ions which ensured charge-compensation, as required in these materials¹. Two cells were employed for each fluoride in order to obtain Er^{3+} concentrations in the CaF_2 layers from 0.1 to 50 mol% by simply varying the ErF_3 temperature (900C-1130C), the CaF_2 temperature being kept constant at 1210C and ensuring a growth rate of 0.5 $\mu\text{m}/\text{h}$. The Er concentration could be inferred by assuming that the entire ErF_3 flux caused an effective Er incorporation in the crystalline lattice of the growing CaF_2 matrix ; indeed, this was later confirmed by Rutherford backscattering measurements. The Er molar fraction in the doped

layers was calculated from the molar cation ratio : Er / (Er+Ca). Layer thickness was generally set at 2 μm .

Reflection high energy electron diffraction (RHEED) observations were performed after epitaxy in order to assess layer crystallinity. Whatever the growth temperature and Er concentration investigated, the diffraction patterns were found to typically correspond to that of the substrate surface, therefore to monocrystalline (100) $\text{CaF}_2\text{:Er}^{3+}$ epitaxial layers.

Photoluminescence spectra of the samples were obtained at 77 K in a closed cycle He cryostat. Photoluminescence spectroscopies were investigated in two spectral ranges : [0.83-0.86 μm] and [1.5-1.6 μm] involving the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ and the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ Er^{3+} ions transitions. Excitation in the $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ absorption band of Er^{3+} ions was performed with the 514.5nm line of an Ar^+ laser. A Ti-sapphire laser tuned at 780nm was used to obtain the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ transition.

3. Results and discussion :

In a first step, because growth temperature is a parameter of major importance in molecular beam epitaxy, its influence on the optical properties of the $\text{CaF}_2\text{:Er}$ layers had to be investigated. Growth temperatures of 450, 520 and 600°C were therefore considered, as this is the range used for CaF_2 epitaxy. The photoluminescence spectra obtained in the near infrared region around 850nm are shown in Fig.1 for a CaF_2 layer with a 0.6 mol% Er^{3+} concentration. The different peaks were assigned by taking the emission centers in $\text{CaF}_2\text{:Er}^{3+}$ bulk material² as reference. As depicted in fig.1, the emission peaks observed in the MBE Er-doped CaF_2 layers were all found to correspond to the emissions already reported in $\text{CaF}_2\text{:Er}^{3+}$ bulk crystals irrespective of the growth temperature. With respect to the isolated centers, two centers were identified¹ : C_{4v} and C_{3v} symmetry sites in which the interstitial F^- ion is in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions respectively. In addition, different aggregate centers, which were labelled C, D(1a) and D(2a) in bulk materials, were also found to be present.

As was also found in bulk materials, the relative distribution between the different Er^{3+} centers appears was very sensitive to growth conditions. Indeed, the optimal temperature range for the single Er^{3+} centers appears to be 500-520°C. This result is in good agreement with has already been found for Nd doped CaF_2 layers grown by the same technique³. When decreasing or increasing the growth temperature from this optimum, the emission intensity associated with the aggregate centers increased.¹ It is worth noting that growth temperature more markedly affects the layers with low Er contents.

With respect to the 1.54 μm emission, the photoluminescence spectra exhibit a significant emission intensity only for concentrations higher than 1%. For that emission line, no relevant difference was noted when the growth temperature was varied between 520°C and 600°C, but a slight increase was found however to the benefit of the former temperature. This is why this growth temperature was subsequently used.

In a second step, the effect of Er concentration was investigated in the two wavelengths considered on a series of CaF_2 layers grown with different Er^{3+} concentrations ranging from 0.05 to 50 mol%.

Figure 2(a) shows the behaviour of the emission spectra around 850nm as a function of Er^{3+} concentration. The spectra exhibit the emission lines corresponding to the different sites involved, as discussed previously. Within the lower range of Er concentration (<6 mol%), the intensity of the emission lines associated with the single Er^{3+} centers and the aggregate center labelled C decrease rapidly relatively to the complex D(1a) and D(2a) ones, whose intensity

increases monotonously with the Er content⁴. When the Er concentration exceeds 6 mol%, the main emission was observed to correspond to the D(2a) center.

Figure 2(b) shows the emission spectra for the previous series of layers in the 1.55 μm range. As can be seen, there exist some weak peaks together with a sharp emission line at 1.54 μm , for the whole Er concentration range. The wavelengths of the emission lines and their relative intensity do not markedly change over the concentration range studied.

The emission related to the D(2a) center (0.84 μm) and the 1.54 μm emission behave in the same way, which suggests that the line at 1.54 μm would be associated with this type of aggregate centers.

Finally, the integrated emission around 1.54 μm was studied as a function of the Er concentration. As shown in Fig.3, the intensity was observed to increase as long as the Er concentration had not reach 35 %. Beyond 35% photoluminescence quenching occurred for the IR emission due to the energy transfer between close ions. This has been supported by an up-conversion study to be published elsewhere. So far, this optimum concentration is the higher value reported.

5. Conclusion

For the first time, it has been shown that $\text{CaF}_2\text{:Er}^{3+}$ thin films can be grown by Molecular Beam Epitaxy with Er concentrations up to 50 mol% without noticeable degradation of the layer crystallinity. Close control of the doping level was achieved by varying the flux of ErF_3 .

Photoluminescence measurements were used to study the influence of growth temperature and Er ions concentration on the incorporation of Er^{3+} ions in CaF_2 . The optimal range temperature was found to be 500-520°C. Emission lines from aggregate Er^{3+} ions centers became dominant and rose as the Er concentration increased.

The centers involved in the IR emission behave as aggregate centers. Quenching of the integrated luminescence intensity for the 1.54 μm emission occurred at 35 mol% Er^{3+} .

To our knowledge, these are the highest values reported for Er-doped materials showing the capabilities of the MBE technique for growing Er-doped layers emitting at 1.54 μm , which is the standard wavelength in optical telecommunications.

Acknowledgements : The authors are grateful to G. Lacoste for technical assistance, and M.Dupuy and F.Pierre (CENG - Grenoble) for RBS measurements.

[1] E. Daran, L.E. Bausá, A.Muñoz-Yagüe and C. Fontaine, *Appl. Phys. Lett.* **62**, (1993).

[2] D.R. Tallant and J.R. Wright, *J. Chem. Phys.* **63**, 2074 (1975).

[3] L.E. Bausá, R.Legros and A.Muñoz-Yagüe, *Journal de Physique IV*, 297 (1991).

[4] E. Daran, L.E. Bausá, A.Muñoz-Yagüe and C. Fontaine, to be published in *J. Appl. Phys.* in March, 1994.

Fig.1. Photoluminescence spectra of three (100) $\text{CaF}_2:\text{Er}$ layers. Er concentration is 0.6 mol% and growth temperature : (a) 520°C, (b) 450°C and (c) 600°C.

Figure 2 : Er^{3+} luminescence spectra for the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ (a) and $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ (b) transitions at 77K for CaF_2 layers with different Er^{3+} contents : (1) 45.6 ; (2) 35.4 ; (3) 23.5 ; (4) 8.7 ; (5) 1.8 mole % Er^{3+} .

Figure 3 : Integrated emission intensity in the 1.54 μm region at 77K as a function of Er^{3+} concentration for the MBE $\text{CaF}_2\text{:Er}$