INFRARED TO VISIBLE LUMINESCENCE UPCONVERSION BY $\text{Yb}^{3+} \rightarrow \text{RE}^{3+}$ ENERGY TRANSFER IN β'' -ALUMINA ($\text{RE}^{3+} = \text{Er}^{3+}, \text{Ho}^{3+}, \text{Tm}^{3+}$)

B. VIANA, L.A. MOMODA* and B. DUNN*

Laboratoire de Chimie Appliquée de l'Etat Solide, UA 1466 CNRS ENSCP, 11 rue P & M Curie, F-75231 Paris cedex 05, France

**Laboratory of Materials Science and Engineering, School University of California, Los Angeles, CA 90024, USA*

Abstract - Beta"-alumina crystals containing mixed Yb^{3+} - RE^{3+} ($\text{RE}^{3+} = \text{Er}^{3+}, \text{Ho}^{3+}, \text{Tm}^{3+}$) pairs are synthesized by ion exchange techniques. Under a 970nm excitation from a C.W. Ti-sapphire laser, a fluorescence is observed in the visible range with the three codoped samples. This work presents the efficiency results in the β'' -alumina matrix. The mechanism and upconversion efficiencies for the Yb^{3+} - Er^{3+} systems are discussed as well as the choice of the host for the upconversion mechanisms. A good matrix should have the capacity to be doped with a high concentration of rare earth ions and to have low phonon energies to discourage non-radiative and to encourage radiative processes.

1.- Introduction

Several recent works on upconversion have renewed the interest of emitting light system at shorter wavelength than the pump light. Such phenomenon, called upconversion luminescence, was first reported using infrared light from flashlamps to excite $\text{Yb}^{3+}/\text{I}^-$. Nowadays, the growing market of the powerful near infra-red laser diode increases the interest of efficient upconverting systems. In the blue-green range, there is a need of new stimulated emission for military applications (target illumination and designation, laser radar) or optical data storage, code bar reading as well as for medical procedure.

Sodium beta"-alumina has long been known for its ion transport properties but this matrix is also well known as a unique host for rare-earth ions [2]. Doped with rare-earth ions, this host presents some very large emission and absorption bands which make this material very interesting for the energy transfers. The starting material has a layered structure consisting of spinel blocks separated by conduction planes. In the conduction planes, Na^+ could be readily replaced by other cationic species by ion exchange techniques [2].

This short paper presents the optical properties of Na^+ - β'' alumina doped with Yb^{3+} and RE^{3+} ($\text{RE}^{3+} = \text{Er}^{3+}, \text{Ho}^{3+}, \text{Tm}^{3+}$) using a procedure as described in [3]. For a sake of clarity, mainly the Er^{3+} luminescence in the Er, Yb system will be detailed.

2.- Results

2.1 Yb->Er energy transfer

Under a 970nm excitation wavelength produce from a Spectra-Physics Ti-Sapphire laser and corresponding to the $\text{Yb}(^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2})$ transition, a visible luminescence is observed from the three RE, Yb β'' :alumina systems. Fig 1 represents the emission spectrum in $\text{Na}_{0.73}\text{Yb}_{0.28}\text{Ho}_{0.03}\text{Mg}_{0.67}\text{Al}_{10.33}\text{O}_{17}$. This crystal contains a strong Yb^{3+} concentration to insure a good Yb-> Er energy transfer. A strong green (550nm) and red (650nm) emission is observed, relieving the presence of A.P.T.E. (Addition de Photons par Transfert d'Energie) [4,5]. On the same graph, the dash line represents the emission spectrum of this sample under a 488nm excitation in the $^2\text{H}_{11/2}$ and

Fig 1: Visible emission spectra of Yb-Er β'' -alumina under 970nm excitation (solid line) and 488nm excitation (dashed line)

$^4F_{7/2}$ levels. The two spectra are normalised for the green emission. In that case, a strong intensity difference is noticed on this picture for the red emission around 650nm with the two different excitations.

The upconversion processes are characterized by the intensity measurements of the visible emitted light with the variation of the near infra-red laser source. A relation as $I_{vis} = (I_{NIR})^n$ characteristic of a n-photons processus is expected. When plotted against the near infra-red excitation in a log-log scale, the intensity variation at 550nm and 650nm give a slope of 1.9 ± 0.2 indicating a two photons mechanism.

Fig 2 presents a schematic diagram of the upconversion mechanism producing the visible light. First, the near IR energy absorbed by Yb^{3+} is transmitted from the $Yb(^2F_{5/2})$ level to the $Er(^4I_{11/2})$ level in good resonance. Then the two-photon processes presented on this picture lead to the green (Fig2a) and red emission (Fig2b). As the $Er(^4I_{11/2})$ level presents a lifetime of approximately 60 μ s, a value too low to correspond to a good metastable level acting as a storage reservoir for the pump lamp, non-radiative deexcitation can occur to the metastable $^4I_{13/2}$ level ($\tau=10$ ms). The $^4F_{3/2}$ emitting level is populated from the $^4I_{13/2}$ level as shown in Fig2b. The other possible mechanism to populate the $^4F_{9/2}$ level -a non-radiative deexcitation from the $^4S_{3/2}$ level- is precluded because of the strong intensity difference noticed for the red emission. These processes explain the relative strong red emission observed under 970nm excitation.

2.2 Efficiency in the Yb,Er system

The efficiency of the A.P.T.E. mechanism is determined from $E = \frac{I_{vis}}{I_{IRabs}}$ where I_{vis} represents the total emitted light in the visible range and I_{IRabs} the intensity of the 970nm excitation source absorbed by the sample. The later intensity can easily be estimated from the absorption cross section measurement while the former is estimated with a calibrated photomultiplier as described in /6/. The experimental efficiency values for the Yb-Er system are $5.7 \times 10^{-6} \text{ cm}^2/\text{w}$ and $2 \times 10^{-5} \text{ cm}^2/\text{w}$ at respectively 545nm and 650nm. The measured cw values are divided by the power density of the 970nm beam, 0.54w/cm² to allow comparisons of these values to those reported in the other hosts. In table 1 are presented some values of the measured efficiencies for inorganic materials doped with the same ions. The efficiencies in the β'' -alumina matrix are much lower than those reported in fluoride systems but stronger than in glasses.

Fig 2: Upconversion mechanisms producing (a) green and (b) red emission in Yb-Er β'' -alumina

The strong non-radiative deexcitation by multiphonon in the β'' -alumina matrix already mentioned with other trivalent rare-earth ions [7] precludes the obtention of high efficiencies. On the contrary, the long lifetime of the $\text{Er}(^4\text{I}_{13/2})$ level give a good efficiency for the red emission at 650nm.

Table 1: Measured Upconversion efficiencies for various hosts doped with Yb^{3+} and Er^{3+}

Host Material	Emission Wavelength,nm	E cm^2/W	reference
$\text{Y}_{0.8}\text{Yb}_{0.19}\text{Er}_{0.01}\text{F}_3$	550	2.8×10^{-1}	(8)
	650	2.8×10^{-2}	
$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Yb,Er}$	540	1.1×10^{-4}	(4)
	650	3.4×10^{-4}	
$\beta''\text{-Alumina}:\text{Yb,Er}$	545	0.6×10^{-5}	
	650	2×10^{-5}	
Silicate Glass:Yb,Er	540	2×10^{-7}	(9)

3.- Conclusions

The β'' -alumina host presents some very large emission and absorption bands and the multisite nature of this host provides a good spectral overlap which make this matrix very interesting for the energy transfers and therefore the infrared to visible upconversion. Visible luminescence is observed from the three Yb,RE β'' -alumina systems. In particular, codoped with Yb^{3+} and Tm^{3+} a strong near infrared luminescence is observed (see fig3) with an interesting blue emission centered at 470nm and corresponding to a 3-photons process. However the high nonradiative rates of the oxygen based lattice dominate the upconversion processes and lead to a low efficiency to the blue emission of Tm^{3+} and to the green emission of Er^{3+} .

Fig 3: Visible emission spectrum of Yb-Tm β "-alumina under 970nm excitation. The curve is corrected for the apparatus response.

References

- /1/ JOHNSON, L.F., GUGGENHEIM, H.J., Appl. Phys. Lett. 19 (1971) 44
- /2/ DUNN, B., FARRINGTON, G.C., Solid State Ionics 9&10 (1983) 223
- /3/ MOMODA, L.A., BARRIE, J.D., DUNN, B., Mat. Res. Bull. , 24 7 (1989) 859
- /4/ AUZEL, F., Proc IEEE 61 (1973) 758
- /5/ WRIGHT, J.C., FONG, F.K., Ed Springer-Verlag N-Y (1976) 239
- /6/ YEH, D.C., SIBLEY, W.A., SUSCAVAGE, M., DREXHAGE, M.G.,
J. Appl. Phys 62 (1987) 266
- /7/ VIANA, B., DAI, H., DUNN, B , MOMODA, L.A., NISHIDA, F., STAFSUDD, O.M.,
Chem. Phys. Letters (to be published-1991)
- /8/ AUZEL, F., PRICILE, D., J. Lumin. 8 (1973) 32
- /9/ CHAMARRO, M.A., CASES, R., J. Lumin. 42 (1988) 267