

## SOME OPTICAL PROPERTIES OF $\text{Yb}^{2+}$ IONS IN $\text{YbF}_3$ -DOPED $\text{CaF}_2$ CRYSTALS

Irina Nicoara, Marius Stef and Andreea Pruna

*Dept. of Physics, West University of Timisoara, 300223 Timisoara, Romania*

### **Abstract**

Various  $\text{YbF}_3$ -concentration calcium fluoride crystals have been grown using the vertical Bridgman method. Room temperature absorption and emission spectra of the divalent ytterbium ions have been investigated. The influence of  $\text{PbF}_2$ ,  $\text{LiF}$  and  $\text{NaF}$  codoping on the  $\text{Yb}^{3+} \rightarrow \text{Yb}^{2+}$  conversion and on the spectroscopic properties have also been studied.

**Keywords:** Laser materials, Rare-earth, Spectroscopic properties.

### **1. Introduction**

In the last time the interest in  $\text{YbF}_3$  -doped  $\text{CaF}_2$  crystals used as laser material is still growing due to the well known good optical characteristics of the  $\text{CaF}_2$  host. The Ytterbium ions are most easily stabilized as trivalent ions in  $\text{CaF}_2$  crystals, but the divalent state has certain distinct advantages for laser applications [1, 2]. The change of valence has been attained by baking the crystals in a suitable atmosphere [3], by electrolytic coloration or exposing them to ionizing radiation [3, 4]. The properties of  $\text{Yb}^{2+}$  ions have been less investigated than the properties of the trivalent Yb.

In this work we report the growth and some optical properties of  $\text{YbF}_3$ - doped  $\text{CaF}_2$  crystals with high divalent Yb ions concentration obtained without any other treatment. The influence of the  $\text{Pb}^{2+}$ ,  $\text{Li}^+$  and  $\text{Na}^+$  ions on the optical absorption spectra and emission spectra of the  $\text{Yb}^{2+}$  ions have been investigated. The presence of the  $\text{Li}^+$  and  $\text{Na}^+$  ions drastically decreases the absorption coefficient of the characteristic absorption in the UV domain of the divalent ytterbium. The emission spectra are also influenced by these ions.

### **2. Method and samples**

Various  $\text{YbF}_3$  concentration doped calcium fluoride  $\text{Ca}_{1-x}\text{Yb}_x\text{F}_{2+x}$  ( $x = 0.0007 - 0.016$ ) and  $\text{PbF}_2$ ,  $\text{LiF}$ , and  $\text{NaF}$ -codoped crystals have been grown using the conventional Bridgman technique [5]. Room temperature optical absorption spectra have been obtained using a Shimadzu 1650PC spectrophotometer. Room temperature emission spectra have been recorded using a Perkin Elmer LS 55 spectrofluorimeter.

### 3. Results and Discussions

The optical absorption spectra of the crystals exhibit intense UV absorption bands, characteristic for divalent Yb ions. It is known that the optical properties of the crystals depend on the  $\text{Yb}^{2+(3+)}$  and  $\text{F}^-$  ions positions in the lattice. The  $\text{Yb}^{3+}$  ions substitute for  $\text{Ca}^{2+}$  ions in the lattice and need charge compensation obtained by an interstitial  $\text{F}^-$  ion located in various positions giving rise to a rich multisite structure, which leads to broad absorption and emission bands. The  $\text{Yb}^{2+}$  ions substitute for  $\text{Ca}^{2+}$  ions, do not need charge compensation and possess cubic symmetry; the characteristic absorption bands are:  $A_i$  ( $i=1, 2, 3, 4$ ), (Figs.1, 2, 3 and 5) [1-4, 6, 7].

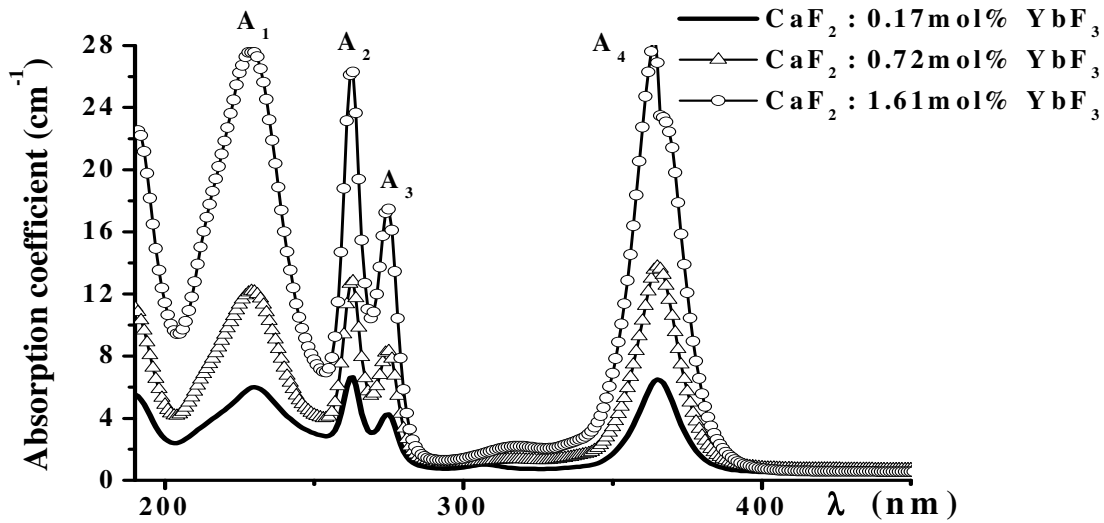


Fig. 1. Influence of  $\text{YbF}_3$  concentration on the absorption spectra.

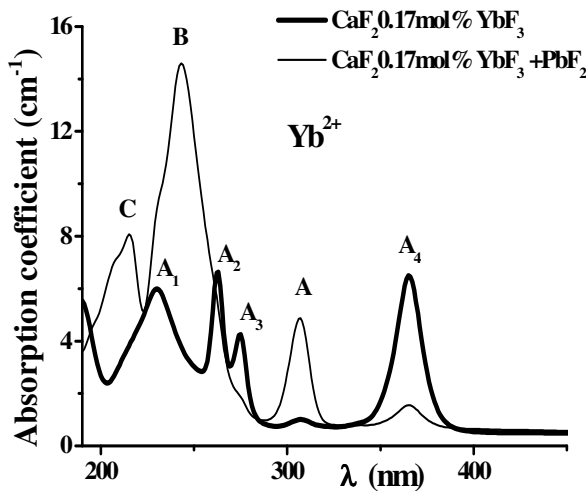


Fig. 2. Influence of  $\text{Pb}^{2+}$  ions on the absorption spectra.

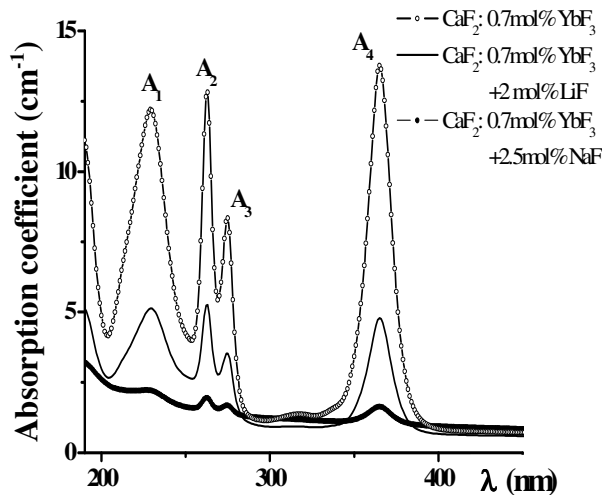


Fig. 3. Influence of  $\text{Li}^+$  and  $\text{Na}^+$  ions on the absorption spectra.

The three types of codoping ions decrease the intensity of the absorption bands of  $\text{Yb}^{2+}$  ions.

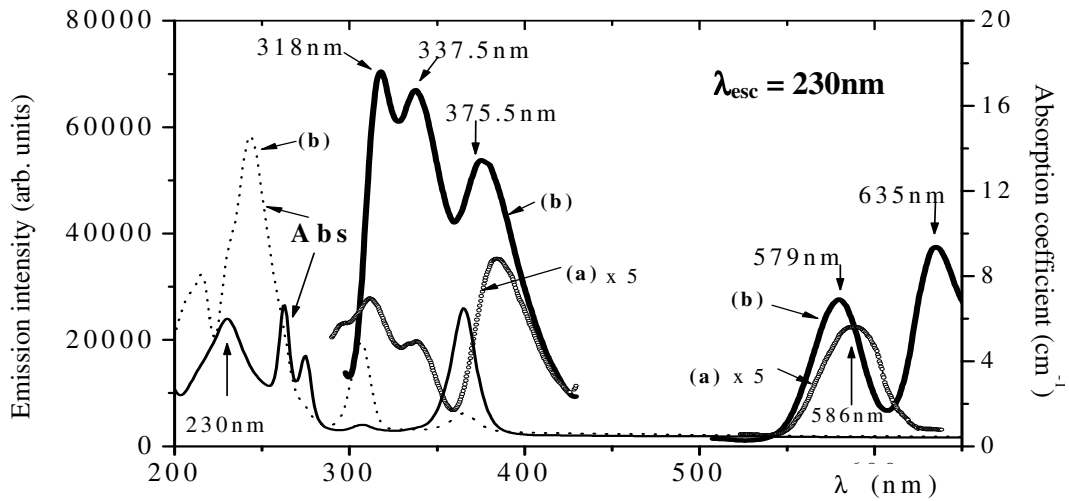


Fig. 3. Influence of the  $\text{Pb}^{2+}$  ions on the emission spectra: (a)  $\text{CaF}_2:0.17\text{mol}\% \text{YbF}_3$ , five times enlarged, (b)  $\text{PbF}_2$ -codoped  $\text{CaF}_2:0.17\text{mol}\% \text{YbF}_3$ ; absorption spectra are also displayed.

The emission spectra of all samples consist of two broad bands, one in near UV-domain (not reported before), and another in the visible spectral domain. (figs. 3 and 4). A strong influence of  $\text{YbF}_3$  concentration and codopant type on the emission spectra has been observed. The strongest emission intensity has been obtained for  $\text{CaF}_2:0.17\text{mol}\% \text{YbF}_3$  sample codoped with  $\text{PbF}_3$ , ten times stronger than for un-codoped sample (fig.3). The codoping with  $\text{Li}^+$  or  $\text{Na}^+$  ions decreases the emission intensity, too (fig.4). Taking into account the characteristics of the observed emission spectra (large Stokes shift and width of the bands), we assign these emission to the “anomalous luminescence”. The emission bands observed in near-UV domain at room temperature have been not reported before; in all the other luminescence experiments [1-4, 6] the samples have been excited only in the 360nm absorption band at low temperature.

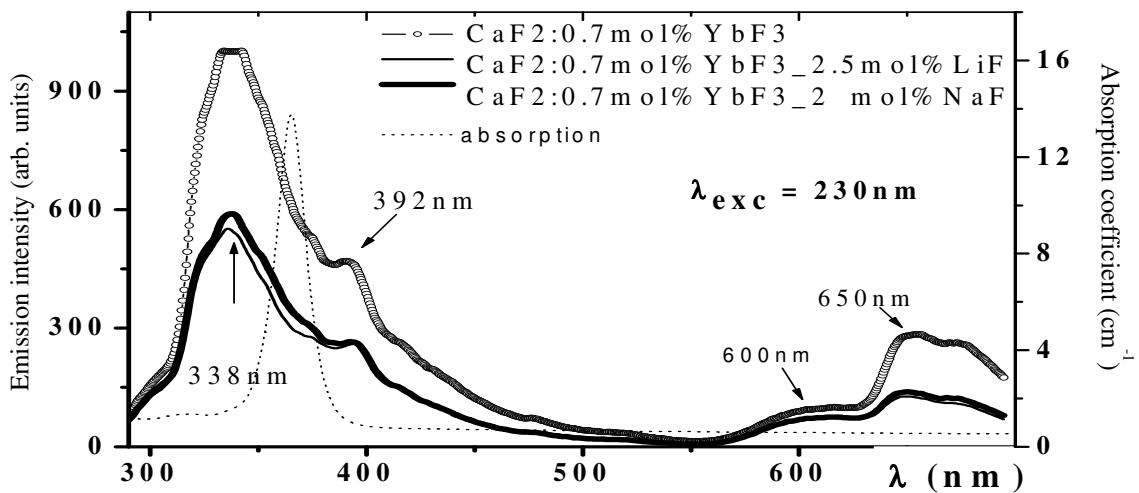


Fig. 4. Influence of the  $\text{Li}^+$  and  $\text{Na}^+$  ions on the emission spectra.

Table 1. Comparison of some data on the optical properties of Yb<sup>2+</sup> ions in CaF<sub>2</sub>.

This work Absorption		Other works		Eremin [7] calculation
		[6]	[3]	
$\lambda$ (nm)		Absorption bands $\lambda$ (nm)		$\lambda$ (nm)
A <sub>4</sub>	365	365	(A)360	364.2, 361
A <sub>0</sub>	307	308	(B) 315	
A <sub>3</sub>	275	273	(C) 271	275
A <sub>2</sub>	263	262	(D) 260	260
E			(E) 234	232
A <sub>1</sub>	230	225	(F) 227	229, 224, 220
G	214	213.6	(G)214	216, 209
Emission $\lambda$ (nm)		Emission $\lambda$ (nm)		
291,312,389 588,579,635		570 (113K)	535 565	

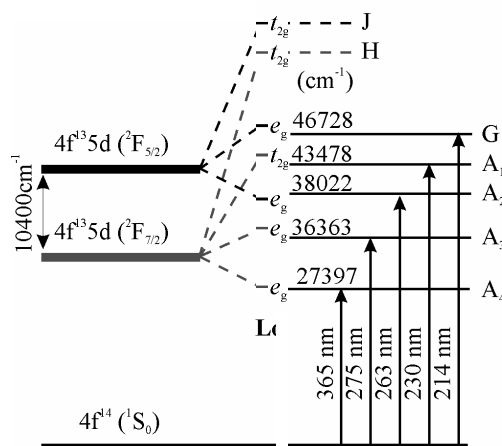


Fig. 5. Energy level diagram for Yb<sup>2+</sup> ions in CaF<sub>2</sub> host.

#### 4. Conclusions

Room temperature optical absorption spectra reveal the existence of both Yb<sup>2+</sup> and Yb<sup>3+</sup> ions. The luminescence studies reveal a strong concentration and codopant dependence of the emission bands. Besides the reported visible luminescence, which is red-shifted now, new emission bands have been observed in near-UV spectral domain, not reported before. The observed emissions are assigned to “anomalous luminescence”.

#### Acknowledgements

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