



On luminescence and energy transfer in oxyapatite co-doped with Eu^{3+} and Tb^{3+} ions.

D. Fahmi

Department of chemistry, Faculty of Sciences, Abdelmalek Essadi University Tétouan Morocco

Received 19 Apr 2016, Revised 01 Oct 2016, Accepted 04 Oct 2016

*Corresponding author. E-mail: drissfahmi@gmail.com. Tél: 212664525820

Abstract

Luminescence properties of oxyapatite co-doped $\text{Ca}_{8.9}\text{Tb}_1\text{Eu}_{0.1}(\text{PO}_4)_6\text{O}_{0.45}[\]_{1.55}$ with europium and terbium was studied, a comparative study of oxyapatites doped with only Eu^{3+} , Tb^{3+} or both of these two ions, was conducted under laser excitations lines at 488 nm, 457.9 nm and 337.1 nm. Using a characteristic transition in the Europium ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0,1,2}$ and Terbium ${}^5\text{D}_4 \rightarrow {}^7\text{F}_{5,4,3}$ spectra at 77 K. A significant energy transfer from Tb^{3+} to Eu^{3+} was evidenced for the co-doped oxyapatite. Such energy transfer seems to occur via different mechanisms which involve particularly high levels of the ion Tb^{3+} (${}^5\text{D}_3$ or above).

Keywords: Luminescence, energy transfer, oxyapatite, fluorescence, terbium, europium

1. Introduction

Rare-earth doped oxyapatites are well known in applied science field as luminescent materials or as sensor of temperature. Recently a wide range of rare-earth doped oxyapatites have been synthesized. In order to enhance luminescence of these materials a second rare-earth ion was introduced in the lattice of the oxyapatites. The general formula of these compounds is $\text{Ca}_{10-x}\text{RE}_x(\text{PO}_4)_6\text{O}_{1+x/2}[\]_{1-x/2}$ ($0 \leq x \leq 2$) where RE is rare-earth ions. In previous work, luminescence with the presence of these two kinds of ions in particular the europium and terbium was studied [1]. This may improve the energy transfer in these oxyapatites under laser excitations. This energy transfer between Tb^{3+} and Eu^{3+} has been the subject of several studies in other materials [2] [3] [4] [5] [6] [7].

The most useful energy transfer from this kind of materials is the fluorescent tubes light given by $(\text{Ca}, \text{Sb}^{3+}, \text{Mn}^{2+})_5(\text{PO}_4)_3\text{F}$ [8], this occurs when the luminophor is excited by the wavelength 253.7 nm (mercury line radiation), the absorption takes place in Sn^{3+} ion and not in Mn^{2+} or in the framework. This luminescence is composed with the blue and yellow emission from Sn^{3+} and Mn^{2+} respectively via the transfer of energy from Sn^{3+} to Mn^{2+} .

In this paper, we present the experimental results obtained on oxyapatites doped with both europium and terbium. Energy transfer between Eu^{3+} and Tb^{3+} co-doped oxyapatite $\text{Ca}_{8.9}\text{Tb}_1\text{Eu}_{0.1}(\text{PO}_4)_6\text{O}_{0.45}[\]_{1.55}$ was carried out through 2 steps procedure, first to excite the ${}^5\text{D}_4$ level of terbium by the blue line (488 nm/20492 cm^{-1}), and then to register the europium fluorescence by energy transfer. In addition, we studied the oxyapatite luminescence after excitation of higher levels of terbium by the yellow line 337.1 nm generated from nitrogen laser.

The aim of this study is to show that under such conditions of excitation, it is possible to improve the emission of Eu^{3+} by energy transfer from Tb^{3+} when concentration of terbium is high in this oxyapatite. This will occur if there is resonance, in other words, if one energy level of terbium corresponds to the same level of Tb^{3+} , or transition of Tb^{3+} ion can raise the Eu^{3+} ion to a higher or the same level according to the energy diagram of the two ions in **figure 1** [9].

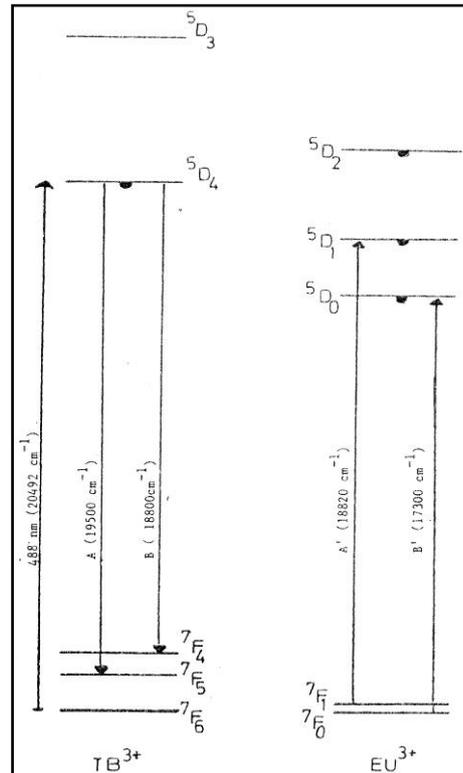


Figure 1: diagram of the first energy levels of Tb³⁺ and Eu³⁺ ions.

These conditions are satisfied with small extra energy provided by phonons through the following pairs of transitions:

- Emission ⁵D₄ ----- ⁷F₅ of terbium, absorption ⁷F₁ ----- ⁵D₁ of europium.
- Emission ⁵D₄ ----- ⁷F₄ of terbium, absorption ⁷F_{0,1} ----- ⁵D₀ of europium.
- Emission ⁵D₃ ----- ⁷F₂ du terbium, absorption ⁷F_{0,1} ----- ⁵D₂ of europium.

To operate with level ⁷F₁ it's necessary to carried out experiments at room temperature so that this level is populated. Energy transfer between two rare earth ions was widely studied by many authors in different matrix, [10][11][12][13]. L.F. Johnson et al. [14] have presented in their work the energy transfer between Tm³⁺ and Ho³⁺ in CaMoO₄, they conclude that the infrared emission of Tm³⁺ and Ho³⁺ was improved by energy transfer. G. Blasse et al [15] have studied the energy transfer between Ce³⁺ and Tb³⁺ cerium compounds. Other studies were carried out by B. Blanzat et al. [16] and L. Boehn et al. [17] where energy transfer was showed between rare earth (Ce³⁺ and Tm³⁺, Ce³⁺ and Tb³⁺) elements in pentaphosphate and glass structure phosphates compounds respectively. In addition, another well-known example is the improvement of the emission of the Eu³⁺ ion by the transfer of energy absorbed by the ion Tb³⁺ in tungstates and molybdates [18] [19] [20]. However, as most of the properties in solid state, luminiphors characteristics depends on the composition of the material, in particular his percentage of activation, grade of purity and temperature:

- The optimum concentration of active centres is usually situated at values of 10% atomic doping, elsewhere the emission intensity decreases by the effect of Quenching.
- Some luminiphors are extremely sensitive to the presence of impurities (other than S and A), called luminescence poisons.
- Others are characterized by a so-called critical temperature choking luminescence.

Effects of various factors such as temperature, concentration of activator and amount of impurities is shown in **figure 2** [21].

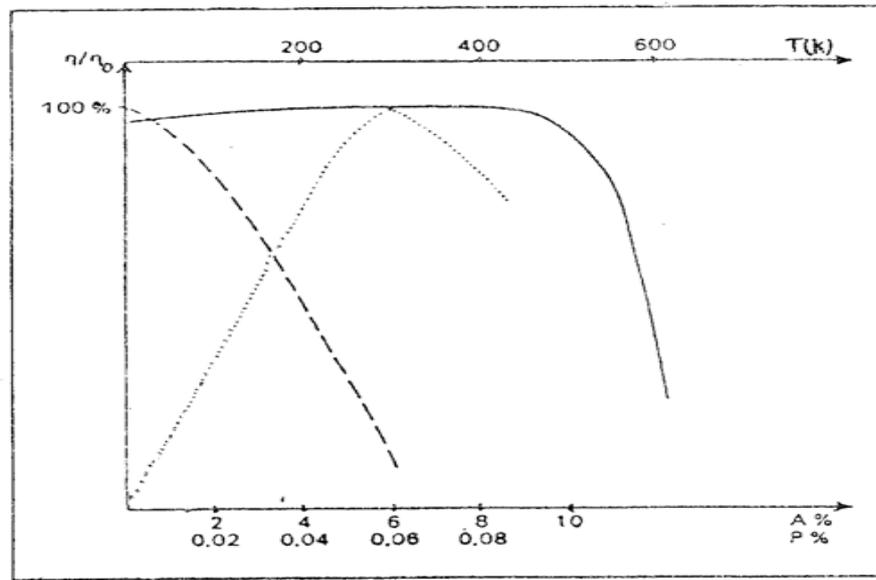


Figure 2: Evolution of the output of conversion with:
 (—) temperature, (....) concentration of activator, (----) amount of impurity P.

To study the energy transfer Tb^{3+} ----- Eu^{3+} in oxyapatites, we carried out experiments in favourable conditions for this phenomenon, without optimization through systematic study of parameters as temperature and concentration of the activator or sensitizer.

2. Materials and methods

A mixture of anhydrous calcium pyrophosphate calcium carbonate and europium oxide with an atomic ratio (Eu+Ca)/P fixed at 1.667 is synthesised in a powder form and it is meticulously crushed and heated at 1350 °C in pure argon atmosphere [22]. The product is annealed at 900 °C under high vacuum; these conditions were maintained until complete cooling, as result of this experimental procedure, monophasic oxyapatites were obtained. These compounds were analysed by X-ray diffraction. All the lines of the diagram can be indexed to the hexagonal system in agreement with the space group P63/m. which is the structure of apatite [23]. Optical studies were performed at 77K, on powders fixed on the inner wall of a Dewar (with no silver or fluorescent varnished) immersed in liquid nitrogen. The excitation of studied compounds was performed with argon ion laser at 488nm and 457.9nm, which allow to selectively exciting terbium in the 5D_4 level as transmitter and europium in the 5D_2 level. The excitation is also carried out at 337.1nm with pulsed nitrogen laser from JOBIN-YVON Company which allows to excite the europium and terbium in higher levels. The excitation spectra were obtained using a colored laser Spectra Physics model 375/376 which is pumped by an argon ion laser (Spectra Physics Model 164).

The spectrometer is a double monochromatic additive PHO from Coderg company, which is controlled by a microprocessor 8 bits (64K RAM), which also control the collection and processing of data. Showed emission is analysed by a spectrometer Jarrell-Ash model 78460 with a focal length of 1 meter and a dispersion of 4.2 Å/m.

3. Results and Discussion

The compounds studied are oxyapatite europium-doped $Ca_{9,9}Eu_{0,1}(PO_4)_6O_{1,05}[]_{0,95}$, terbium doped $Ca_9Tb_1(PO_4)_6O_{1,5}[]_{0,5}$ and oxyapatite co-doped by these two rare earth elements.

The fluorescence spectra of the two compounds were first measured to determine the transitions of the europium and terbium in these matrices in order to understand the energy transfer process Tb^{3+} ----- Eu^{3+} in $Ca_{8,9}Tb_1Eu_{0,1}(PO_4)_6O_{1,55}[]_{0,45}$ compound.

The excitation of these three compounds was performed using the lines at 488 nm and 457.9 nm of an argon ion laser, that selectively possible to excite respectively terbium in the 5D_4 level and europium in the level 5D_2 , and with the line at 337.1 nm from a nitrogen laser that can excite europium and terbium in the upper levels. For excitation spectra, we used a laser Dye, the signal emitted in each case is detected following the procedure previously cited in the Materials and methods. The fluorescence spectra were recorded in the same conditions at 77K.

a) Study under excitation at 457.9 nm and 488 nm:

After excitation at 457.9 nm and 488 nm the spectra obtained at 77K on the compound $Ca_9 Tb_1(PO_4)_6 O_{1.5}[]_{0.5}$ are shown in **figure 3**, Both spectra were recorded in the area from 15500 to 17500 cm^{-1} , corresponding to transitions $^5D_0 \text{-----} ^7F_{0,1,2}$ from europium ion and $^5D_4 \text{-----} ^7F_{4,3}$ from terbium ion.

The spectrum obtained under excitation at 457.9 nm, shows a low emission $^5D_4 \text{-----} ^7F_{4,3}$ from terbium compared with selectively excited spectrum at 488nm: the line at 457.9 nm specific to the excitation of europium, gives in this oxyapatite a very small line at 17500 cm^{-1} which could correspond to the transition $^5D_0 \text{-----} ^7F_0$. But since this line is not excited, compared to the lines $^5D_4 \text{-----} ^7F_4$ of the ion Tb^{3+} , it was attributed to the ion Tb^{3+} .

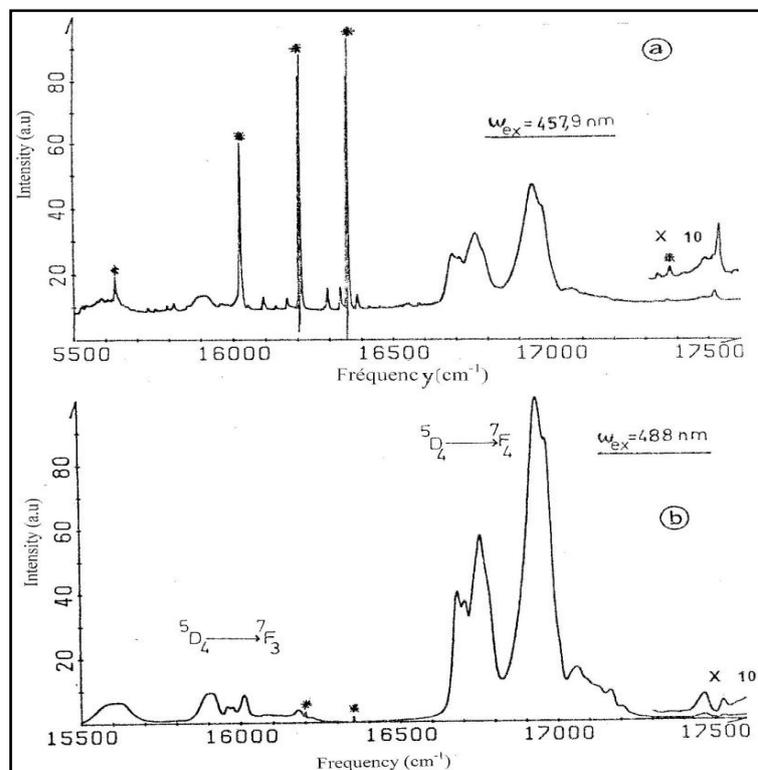


Figure 3: Spectra of fluorescence $^5D_4 \text{-----} ^7F_{3,4}$ of the ion Tb^{3+} of the terbic oxyapatite ($x=1$) at 77K
 (a) Excitation with 457.9 nm, (b) Excitation with 488 nm
 * Parasitic lines of the plasma of the ionized Argon laser

Therefore, we find that $Ca_9 Tb_1(PO_4)_6 O_{1.5}[]_{0.5}$ is pure. But, in the case that contains residual traces of europium, they will not affect the study of the transfer which will follow. A similar purity test was made on the compound doped with europium $Ca_{9,9} Eu_{0,1}(PO_4)_6 O_{1,05}[]_{0,95}$. Spectra of fluorescence, at an excitation wavelength of 457.9 nm, are shown in **figure 4**. It is characteristic of the emission of europium in these oxyapatites namely a line $^5D_0 \text{-----} ^7F_0$ unusually intense and centred at 17500 cm^{-1} and transitions $^5D_0 \text{-----} ^7F_{1,2}$ at high frequencies [24]. While under excitation at 488 nm, the spectrum corresponding to Eu^{3+} ion show very low intensities, and no emission line corresponding to the Tb^{3+} ion was observed. This confirms that this compound is also pure.

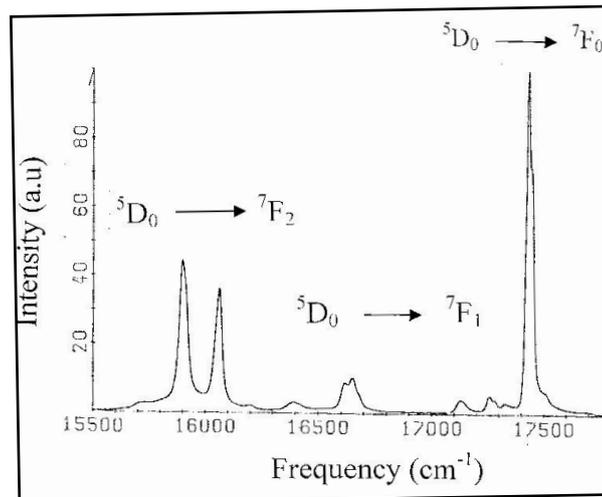


Figure 4: Spectra of fluorescence 5D_0 ----- ${}^7F_{0,1,2}$ of the ion Eu^{3+} in the oxyapatite doped with the europium ($x=0,1$), at 77K and under excitation 457.9 nm

Figure 5 shows the normalized spectra with detail of spectral region situated between 17350 cm^{-1} and 17600 cm^{-1} corresponding to the transition 5D_0 ----- 7F_0 in the europium under on selective excitation (full line) and the two lines of the Tb^{3+} ion (dotted lines). This figure highlights the overlap between the intense band of the Eu^{3+} ion (5D_0 ----- 7F_0) and two weak lines of Tb^{3+} ion (5D_4 ----- 7F_4 or $5D_4$ ----- 7F_5). The displacement of the energy levels of Eu^{3+} ion to higher frequencies and those of the Tb^{3+} ion to lower frequencies does not promote the transfer of energy between these two ions in oxyapatite $Ca_{8,9}Tb_1Eu_{0,1}(PO_4)_6O_{1,55}[O_{0,45}]$ by the process: emission of terbium, europium absorption 5D_4 (Tb^{3+}) and ${}^5D_{1,0}$ (Eu^{3+}) as reported in the literature [25] [26] [27].

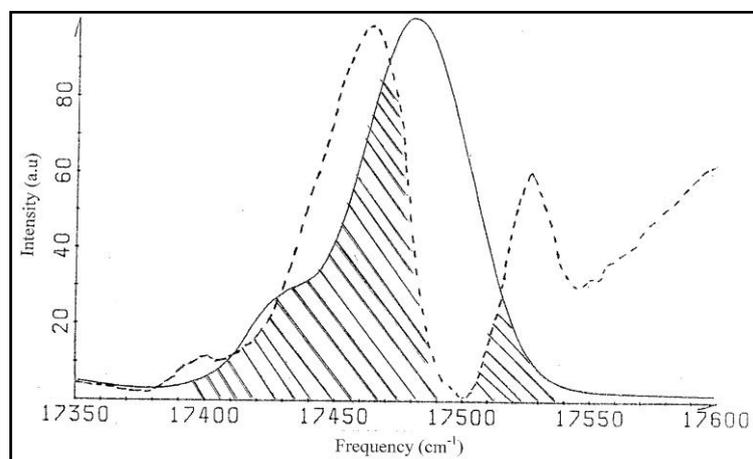


Figure 5: Details with standardized spectra at 77K of the covering of the transition 5D_0 ----- 7F_0 (—) of the ion Eu^{3+} (under not-selective excitation 337.1 nm) with two very weak lines of the ion Tb^{3+} around 17500 cm^{-1} (---) (under excitation 488 nm).

However, the recovery above allows a low energy transfer as shown by the analogy of the excitation spectra (**figure 6**) in the 5D_4 level of Tb^{3+} ions, monitored in the 5D_4 ----- 7F_5 transition of Tb^{3+} ion at 18490 cm^{-1} and 5D_0 ----- 7F_2 transition of Eu^{3+} ion at 16010 cm^{-1} (frequency at which no transition ion Tb^{3+} was observed). Nonetheless, this transfer occurs but is very low, given the low intensity of the spectrum (b) compared to the spectrum (a).

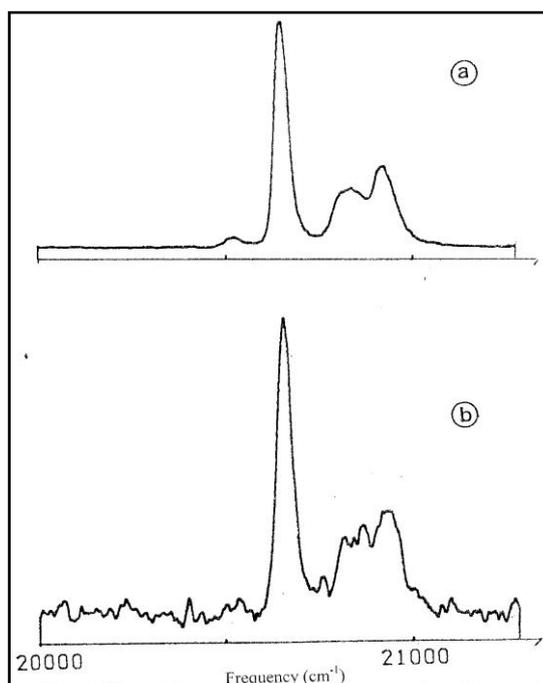


Figure 6: Spectra of excitation at 77K for the observations:
 (a) On the transition ${}^5D_4 \text{-----} {}^7F_5$ of the ion Tb^{3+} at 18490 cm^{-1}
 (b) On the transition ${}^5D_0 \text{-----} {}^7F_2$ of the ion Eu^{3+} at 1601 cm^{-1}

b) Study under excitation at 337.1 nm.

The energy transfer between the ion Tb^{3+} and Eu^{3+} ion in these oxyapatites, from the 5D_4 level (Tb^{3+}) is very low, we consider that this energy transfer could occur between other higher levels of these ions, especially under excitation at 337.1nm (nitrogen laser).

b -1) Study of the oxyapatite $Ca_9 Tb_1(PO_4)_6 O_{1,5}[]_{0.5}$:

The emission spectrum obtained at 77K in the case for this oxyapatite terbic, under excitation at 337,1nm is reported in **figure 7a**. This spectrum corresponds to transitions from the level transmitter 5D_4 to ${}^7F_{6,5,4}$ levels. The most intense spectral line centred on 18500 cm^{-1} (in green) is part of ${}^5D_4 \text{-----} {}^7F_5$ transitions, however, ${}^5D_4 \text{-----} {}^7F_4$ transitions centred around 17000 cm^{-1} are very low intensity.

b-2) Study of the oxyapatite $Ca_{9,9} Eu_{0,1}(PO_4)_6 O_{1,05}[]_{0,95}$:

The fluorescence obtained at 77K for the oxyapatite $Ca_{9,9} Eu_{0,1}(PO_4)_6 O_{1,05}[]_{0,95}$ after excitation with 337,1 nm (29665 cm^{-1}) is reported in **figure 7b**. The spectrum is recorded in the entire visible range. No line issued from the 5D_2 level is observed. Two weak lines registered on about 19000 cm^{-1} are due to the ${}^5D_1 \text{-----} {}^7F_0$ emission, while all the spectrum and particularly the most intense peak centred at 17500 cm^{-1} are characteristics of ${}^5D_0 \text{-----} {}^7F_{1,2}$ emission of the sites B (Eu^{3+} in position II).

However, literature reports predominance of sites A in this kind of oxyapatites [28], it follows that the lines at 337.1 nm selectively excite minority sites.

b-3) Study of the oxyapatite $Ca_{8,9} Tb_1 Eu_{0,1}(PO_4)_6 O_{1,55}[]_{0,45}$:

The oxyapatite presented in this work contains both terbium and europium. The fluorescence registered at 77 K after excitation at 337.1 nm is reported in **figure 7c**; this standardized spectrum is recorded under the same conditions as the previous two spectra. It is composed of emission lines from Eu^{3+} and Tb^{3+} ions.

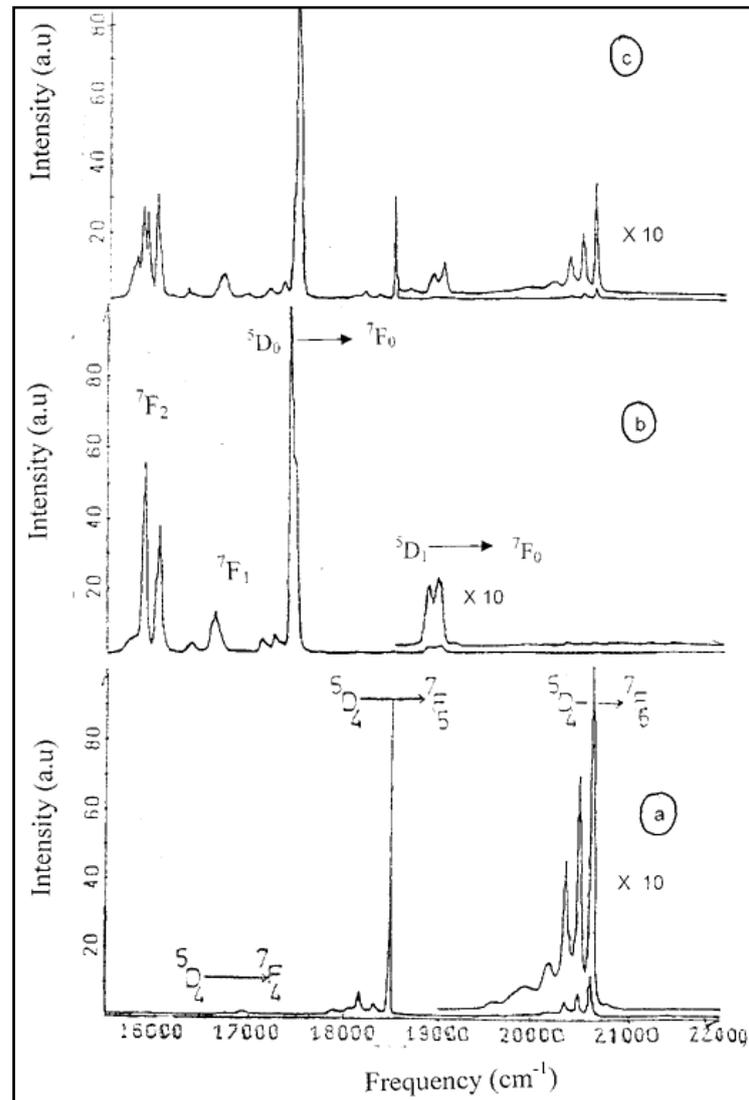
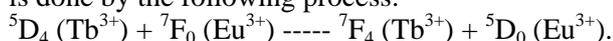


Figure 7: Spectra of fluorescence at 77K under excitation 337.1 nm
 (a) terbic Oxyapatite (x=1), (b) Oxyapatite europic (x=0,1)
 (c) terbic Oxyapatite doped with the europium (x_{Tb}=1, x_{Eu}=0,1)

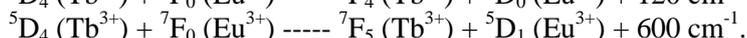
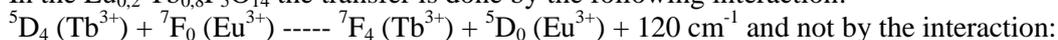
Comparison of this spectrum with the previous ones, show that most of the emission is due to the fluorescence of the Eu^{3+} ion unlike the previous case. It is the emission from A sites of europium, emission on the lines of europium is 20 times more intense than in the case of oxyapatite which did not contain terbium (**spectra b**), while the emission on the lines of the Tb^{3+} ion is 6 times lower than that obtained in oxyapatites which contained only terbium (**spectra a**).

In this oxyapatite, europium contributes strongly to the de-excitation of the ion Tb^{3+} . From this result it is clear that the emission of the Eu^{3+} ion is mainly due to the transfer of the energy absorbed by the ion Tb^{3+} . Without specifying the transitions involved in this transfer and according to the excitation spectra. We can say that the energy transfer takes place only from higher levels of Tb^{3+} ion (level $^5\text{D}_4$).

Given the highly disturbed levels found in oxyapatites structures, energy transfer between Tb^{3+} and Eu^{3+} appears to involve different mechanisms from those given in the literature. For example, in oxysulfures [29], the transfer is done by the following process:



In the $\text{Eu}_{0.2}\text{Tb}_{0.8}\text{P}_5\text{O}_{14}$ the transfer is done by the following interaction:



Conclusion

The study of these three apatite compounds allowed us to show that under excitation at 337.1 nm, emission of Eu^{3+} ion is considerably increased by the transfer of energy absorbed by the ion Tb^{3+} . So that, as we have commented in this work, the emission of europium is 20 times more intense, however, the emission of terbium is 6 times lower.

By this energy transfer, the emission arises from Eu^{3+} ions at sites A in 6h position, however, in the case of direct excitation; the minority sites called B in Eu^{3+} ions are involved. Note that, even if by direct excitation or via of the Tb^{3+} ion in higher levels, the energy transfer between Eu^{3+} ions (sites A and B) is not detectable in the transitions arising from the level $^5\text{D}_0$.

The excitation spectra in the $^5\text{D}_4$ levels of the Tb^{3+} ion show, according to the very small overlap of emission and absorption spectra respectively from Tb^{3+} and Eu^{3+} , that the energy transfer observed mainly involves high levels of the Tb^{3+} ion, mainly $^5\text{D}_3$ or above.

Acknowledgements: The author is grateful to the Professor B. SOUHAIL from University of Tétouan, Morocco, for fruitful discussions and technical assistance.

References

1. B. Piriou, D. Fahmi, J. Dexpert-Ghys, A. Taitai, J.L. Lacout. *Journal of luminescence* 39 (1987) 97–103.
2. Ting Li, Panlai Li, Zhijun Wang, Shuchao Xu, Qiongyu Bai et Zhiping Yang, *Dalton Trans.*, 44 (2015) 16840-16846.
3. S. Som and S K Sharma. *Journal of Physics D: Applied Physics*, 45 (2012) 4.
4. Schierning, G. , Batentschuk, M., Osvet, A., Winnacker, A. *Optical Materials* 48 (2015) 252-257.
5. Carrasco, I., Bartosiewicz, K., Nikl, M., Piccinelli, F., Bettinelli, M. *Journal of luminescence* 132 (2012) 1299-1306.
6. Jun Zhou, Zhiguo Xia, Marco Bettinelli and Quanlin Liu *RSC Adv.*, 6 (2016) 2046-2054.
7. Yang J, Zhang C, Li C, Yu Y, Lin J. *Inorganic chemistry* 47 (2008) 7262-7270.
8. K.H. Bulter, *Pem. Stat. Press. Ed.* (1980).
9. G. Blasse and A. Bril, *Philips Techn. Rev.* 31 (1970) 303.
10. Qingfeng Guo, Libing Liao, Lefu Mei, Haikun Liu, Yun Hai, *Journal of Solid State Chemistry* 225 (2015) 149-154.
11. W.W.Holloway and M.Kestigian, *Journal of Optical of America* 56 (1966) 1171-1174.
12. R. Reisfeld, Y. Eckstein, *J. Non-Crystl.Solids* 11(1973) 261.
13. S. Tanabe, K.Suzuki, N.Soga, T.Handa, *J.luminescence* 65 (1995) 247.
14. L. F. Johnson, L. G. Van Uitert, J. J. Rubin et R.A. Thomas, *Phys. Rev.*133 (1964) A494.
15. G. Blasse, et A. Bril, *J. Chem. Phys.* 47 (1967) 1920.
16. B. Blanzat, J. P. Denis, R. Reisfeld, *Chem. Phys. Lett.*51 (1977) 403.
17. L. Boehn, R. Reisfeld, B. Blanzat, *Chem. Phys. Lett.* 45 (1977) 441.
18. L.G.Van Uitert, R.R. Soden, *J. Chem. Phys.* 36 (1962) 1289.
19. L.G.Van Uitert, *J. Electrochem. Soc.* 1 (1963) 110.
20. L.G.Van Uitert, R.R. Soden, *J. Chem. Phys.*36 (1962) 1797.
21. P. Maestro, P. Dougier, *L'actualité Chimique, juin-juillet* (1982).
22. A. Taitai, J. L. Lacout, G. Bonel, *Ann. Chimie*, 10 (1985) 29.
23. M. I. Kay, R.A. Young, A.S. Posner, *Nature*, 204 (1964) 1050.
24. B. Piriou, D. Fahmi, J. Dexpert-Ghys, A. Taitai, J.L. Lacout. *Inorganica Chimica Acta* 139 (1987) 307.
25. Toshihiro Yamase, Haruo Naruke, *J. Phys. Chem B*, 103 (1999) 8850-8857.
26. Marco Bettinelli, Fabio Piccinelli, Adolfo Speghini, Jumpei Ueda, Stesuhisa Tanabe, *Journal of Luminescence* 132 (2012) 27-29.
27. Jianming, Zhong, Weiren Zhao, Enhai Song, Yongqiang, *Journal of Luminescence* 154 (2014) 204-210.
28. B. Piriou, D. Fahmi, J. Dexpert-Ghys, A. Taitai, J.L. Lacout. *Journal of Luminescence* 39 (1987) 97-103.
29. J. Dexpert, Y. Charriers, *J. Electrochem. Soc.* 132 (1985) 711.