

Rare Earth Luminescence in Phosphogypsum Waste Produced from Phosphate Ore Processing

Ines Hammam-Nasri ^{1,*}, Karima Horchani-Naifer ¹, Mokhtar Férid ¹ and Donatella Barca ²

¹ Laboratory of Physical Chemistry of Mineral Materials and their Applications, National Research Center in Materials Sciences, Technopole Borj Cedria B.P. 73- 8027 Soliman, Tunisia

² Department of Biology, Ecology and Earth Sciences, University of Calabria, Via Ponte Bucci, Cubo 12B, 87036 Arcavacata di Rende (CS), Italy.

Abstract: Luminescence properties of rare earth elements (Eu³⁺, Sm³⁺, and Ce³⁺) were investigated in phosphogypsum waste produced from the phosphoric acid manufacture. The presence of these elements was already confirmed after analysis of the phosphogypsum sample by inductively coupled plasma mass spectrometry, which showed total rare earth content about 350 ppm. The principal aim of this work is to use the photoluminescence technique for identifying 4f ions by the mutual relationship between excitation and emission spectra. The obtained spectra may be used then as reliable references for monitoring rare earth elements during their extraction from phosphogypsum, any time that the inductively coupled plasma mass spectrometry is inapplicable.

To find the most convenient conditions for observing Eu³⁺ emissions, a powder of calcium sulfate doped with europium (CaSO₄: Eu (1%)) was synthesized. After comparison with the emission and excitation spectra of the synthetic gypsum, it was pointed out that the excitation of the phosphogypsum selectively at 466 nm is the most suitable for observing Eu³⁺ emissions. These latter were obtained at 556 nm and 603 nm. Based on literature data, Sm³⁺ and Ce³⁺ emissions in the phosphogypsum were identified. Sm³⁺ lines were obtained at 567 nm and 602 nm after a selective excitation at the ⁴G_{5/2}-⁶H_{7/2} transition (404 nm). Whereas, cerium luminescence was only observed after calcination of the phosphogypsum sample at 900°C. Ce³⁺ emissions were obtained at 305 nm and 326 nm after excitation of the calcined phosphogypsum at 254 nm. The effect of phosphogypsum impurities on the lifetime of rare earth emissions was also discussed.

Keywords: photoluminescence; inductively coupled plasma mass spectrometry; rare earth; phosphogypsum.

Introduction

In industrial processes, where crystallization or precipitation is applied as a separation technique, incorporation of impurities from the solution into the growing crystals is a widely studied topic¹. For instance, phosphoric acid manufacture, based on a sulfuric attack of the mineral ore (apatite), leads to obtaining phosphogypsum waste (PG) which is isolated from the desired acid by filtration. The most common process results in the formation of dihydrate calcium sulfate (CaSO₄.2H₂O) containing various impurities having as origin the phosphate rock. In fact, during the crystallization of this by-product, these impurities already dissolved in the solution, are most probably inserted into the gypsum matrix by replacement of calcium ions. Among these impurities, we are interested herein on rare earth elements (REEs). Previous studies indicated that around 60 to 80% of rare earth pass

from the mineral ore to the phosphogypsum after reaction with sulfuric acid²⁻⁴.

Until recently, the analysis of REEs in environmental materials has found great problems, at least on a more routine scale. The advancement of ICP-MS technique and the more common use of this technique in environmental and biological research since about 1990 have greatly facilitated their study⁵. However, alongside the benefits of this analytical technique (accuracy, sensitivity, speed...), we cannot deny the presence of disadvantages that limit its use (solid sample preparation delicacy, capping risks of the torch/mass spectrometer interface...) especially when analyzing waste solutions obtained during recovery processes. Since our research is interested mainly in phosphogypsum study and its valorization, we decided to use the photoluminescence as an alternative technique allowing rare earth detection and monitoring.

*Corresponding author: Ines Hammam-Nasri

E-mail address: ines_hammam@yahoo.fr

DOI: <http://dx.doi.org/>

The particular electronic configuration of the REE group represents the origin of its interesting spectroscopic properties. Indeed, their luminescence properties result mainly from the radial extension of both $(5s)^2$ and $(5p)^6$ electronic shells which shield the internal 4f electrons from the crystal field (the electronic configuration of trivalent ions of REE is of type $Kr^{46} 4f^n (5s^2 5p^6)$). Absorption and emission spectra are produced by either internal 4f-4f or 4f-5d transitions⁶.

The spectroscopic properties of RE ions can be divided into two categories, depending on the electronic structure of the ion when it is excited⁷. Many of the RE ions, such as Tb^{3+} , Pt^{3+} , and Eu^{3+} , have an emission that arises from electronic transitions between levels of the $4f^n$ configuration. These 4f electrons are well shielded from the crystal field of neighboring ions by the $5s^2$ and $5p^6$ electrons. Accordingly, the host has only a weak influence on the RE energy levels, and the radiative emissions resemble those of the free ion in terms of their narrow spectral width, long excited-state lifetime, and relatively low oscillator strengths. The other type of ions, such as Eu^{2+} and Ce^{2+} , luminesces as a result of a transition between a $4f^{n-1} 5d^1$ excited state and a $4f^n$ ground state. Unlike the line emitters, the 5d excited state is not strongly shielded from the crystal field by the $5s^2$ and $5p^6$ electrons, and therefore, the spectral properties are more strongly affected by the host lattice⁸.

During the last decades, rare earth activated phosphors have attracted the attention of many researchers. Among them we can mention calcium sulfate doped with rare earth ions which showed interesting properties, making of them prospective candidates for many applications (dosimetry, optical storage materials etc.)^{1,9-13}. The luminescent response of these activators (REE) is so efficient that impurity concentration less than 100 ppm in even small samples can be easily detected¹⁴.

Based on literature data and by comparison with the spectra of synthetic gypsum, luminescence technique has been used in this work in order to identify rare earth emissions in the Tunisian phosphogypsum waste with measures of delay times. The main aim of this study is to make of the photoluminescence technique, a reliable qualitative analytical method, by the selection of suitable excitation wavelengths allowing the identification of rare earth elements after every step of phosphogypsum valorization process, in future works. Analysis by inductively coupled plasma mass spectrometry (ICP-MS) was firstly made in order to prove the rare earth presence in the phosphogypsum sample.

Experimental Section

The phosphogypsum (PG) studied in this work have as origin Sfax (Tunisia) stockpiles. ICP-MS analyses were performed at the Department of

Biology, Ecology and Earth Sciences, University of Calabria, Italy. The phosphogypsum sample was powdered in an agate mortar and then dissolved by microwave digestion using a Mars5 microwave apparatus (CEM technologies). About 100 mg (± 0.01 mg) of powder was placed in a microwave vessel with a mixture of Merck "suprapur" quality hydrofluoric acid (6 ml HF), nitric acid (5 ml HNO_3) and perchloric acid (3 ml $HClO_4$), covered and sealed with a cap and subjected to an oven method that consisted of a 15min ramp to 200 °C and a pressure of 600 PSI, then held at temperature for 15 min and then a 15 min cool down. An unclear solution containing some residue was obtained. The content of the vessel was allowed to heat up to 200 °C. Before the complete evaporation of acid, we added 3ml of pure $HClO_4$ and we maintain heating up to 200°C. Before the complete evaporation, 5 ml of HNO_3 (5%) was then added. A clear, colorless solution was finally obtained. This latter was left to cool down gently and made up to a standard volume in a 100 ml volumetric flask with Millipore water in order to prepare the mother solution. External calibration curves were prepared using Perkin Elmer "multi-element Calibration Standard 2 solution" to analyze rare earth elements. Standard reference materials Micaschist (SDC1) were prepared in the same way and were used as unknown samples during the analytical sequence. Concentrations of the elements were compared with certified values to evaluate accuracy and precision of analytical data¹⁵.

Photoluminescence (PL) measurements were recorded on phosphogypsum pellets with Perkin Elmer spectrometer LS55. This device allows recording excitation and emission spectra only in the UV-visible range.

Results and Discussion

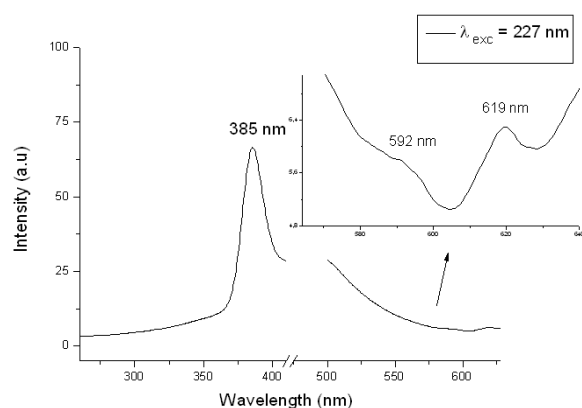
During this study, mainly emissions corresponding to the most intensive transitions (of each element studied) were considered. For example, it is known that luminescence spectra recorded for Eu(III) complexes are those of the $^5D_0 \rightarrow ^7F_J$ ($J = 0-6$) transitions obtained after exciting the $^7F_0 \rightarrow ^5L_6$ transition¹⁶. The f-f transitions of Eu^{3+} consist mainly of a magnetic dipole (MD) and induced electric dipole (ED) transitions. The most intensive transitions of trivalent europium are $^5D_0 \rightarrow ^7F_{1,2,4}$ ¹⁶. Thus, it will be focussed especially on the transitions $^5D_0 \rightarrow ^7F_2$ and $^4G_{5/2} \rightarrow ^6H_{7/2}$ when analyzing, respectively, Eu^{3+} and Sm^{3+} emissions in the phosphogypsum sample.

Europium luminescence

PL of synthetic $CaSO_4$: Eu

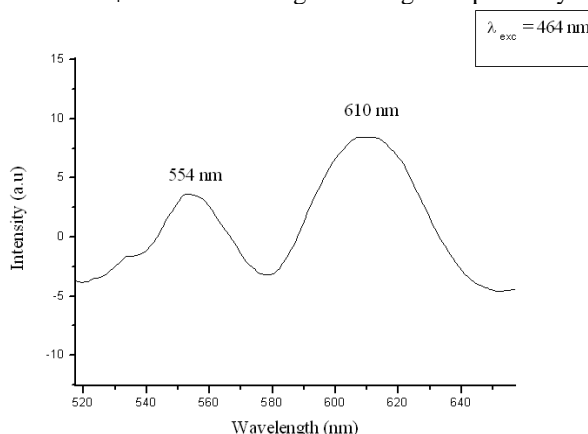
$CaSO_4$ phosphors activated with Eu (1%) were prepared as described by S.V.Godbole et al.¹⁷. Under UV lamp excitation (254 nm) the obtained powder shows a weak red luminescence confirming thus the europium ion insertion within the matrix.

Emission and excitation spectra of Eu doped



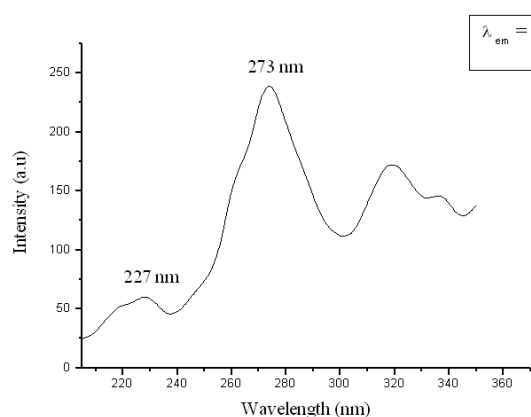
(a)

CaSO₄ are shown in Fig.1 and Fig.2 respectively.

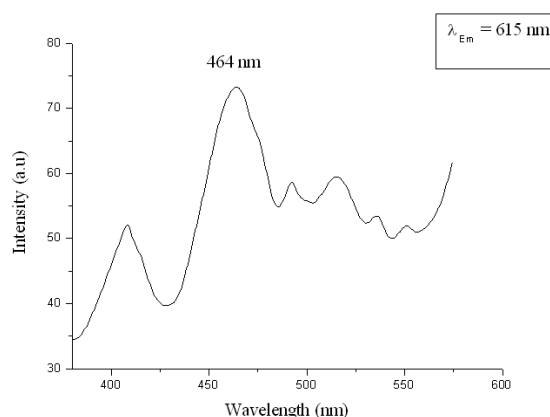


(b)

Figure 1. Emission spectra of CaSO₄: Eu (1%) at a) $\lambda_{exc} = 227$ nm and b) $\lambda_{exc} = 464$ nm.



(a)



(b)

Figure 2. Excitation spectra of CaSO₄: Eu (1%) at a) $\lambda_{em} = 385$ nm and b) $\lambda_{em} = 615$ nm.

Excitation of the phosphor at 227 nm leads mainly to an intense band at 385 nm characteristic of the $4f^6 5d \rightarrow 4f^7$ transition of the Eu^{2+} ion¹² (Fig.1(a)). The weak emissions observed at 592 and 619 nm (Figure.1(a)) are ascribed respectively to Eu^{3+} transitions $^5\text{D}_0 - ^7\text{F}_1$ and $^5\text{D}_0 - ^7\text{F}_2$ ¹⁸. As shown in Fig.1 (b), selective excitation at 464 nm (the resonant wavelength) leads to the observation of emissions at 554 nm and 610 nm respectively ascribed to $^5\text{D}_1 - ^7\text{F}_2$ and $^5\text{D}_0 - ^7\text{F}_2$ transitions of Eu^{3+} ¹⁹.

Excitation spectra of CaSO₄: Eu (1%) at 385 nm and 615 nm show intense bands at 273 nm (Figure 2(a)) and at 464 nm (Figure 2(b)) corresponding respectively to the $\text{O}^{2-} - \text{Eu}^{3+}$ CT transition and to the energy of the $^5\text{D}_0 - ^7\text{F}_2$ transition of Eu^{3+} (the resonant excitation)²⁰.

In the CaSO₄ crystal structure, the Ca^{2+} ions occupy a single crystallographic site (C_{2v} symmetry) with eightfold oxygen coordination¹². In view of the ionic radii of Ca^{2+} (1.12 Å) and Eu^{3+} (1.07 Å) in eight coordination²¹, the Eu^{3+} ion is expected to replace the Ca^{2+} ion in the lattice.

We concluded thus the coexistence of Eu^{2+} and Eu^{3+} ions in the matrix sample. Previous studies^{1,11,17} have linked the conversion of Eu^{3+} to Eu^{2+} either to the excitation wavelength (227 nm) or to the calcination step during the synthesis (600 °C in this work).

Europium emission in the phosphogypsum

The characterization of the Tunisian phosphogypsum by infrared spectroscopy and X-ray diffraction²² showed that it corresponds to the dihydrated phase $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

After having determined the major elements composition in the Tunisian phosphogypsum in a previous work²², we are interested herein to trace elements and precisely to rare earth. Table 1 summarizes the results of the phosphogypsum analysis by ICP-MS and shows a total rare earth content of about 350.21 ppm.

Table 1. Rare earth content in the raw Tunisian phosphogypsum determined by ICP-MS analysis

| Element | Composition (ppm) |
|----------------------|-------------------|
| Y | 80.81 |
| La | 54.42 |
| Ce | 96.73 |
| Pr | 12.71 |
| Nd | 59.42 |
| Sm | 9.63 |
| Eu | 2.29 |
| Gd | 9.55 |
| Tb | 1.46 |
| Dy | 8.94 |
| Ho | 1.81 |
| Er | 5.47 |
| Tm | 0.71 |
| Yb | 5.61 |
| Lu | 0.65 |
| Total content | 350.21 |

In order to identify europium luminescence in the studied sample, its excitation and emission spectra were compared with those of the synthesized $\text{CaSO}_4:\text{Eu}$ studied above (Figure.3 (a) and (b)). Thus, for the Tunisian phosphogypsum, the Eu^{3+} transition $^5\text{D}_1 - ^7\text{F}_2$ is obtained at around 556 nm while the $^5\text{D}_0 - ^7\text{F}_2$ transition is situated at 603 nm.

The excitation resonant band has been well verified after analysis of the sample at $\lambda_{\text{em}} = 616$ nm (Fig.3 (a)). In fact, the obtained spectrum, similar to the reference, showed a band at 466 nm.

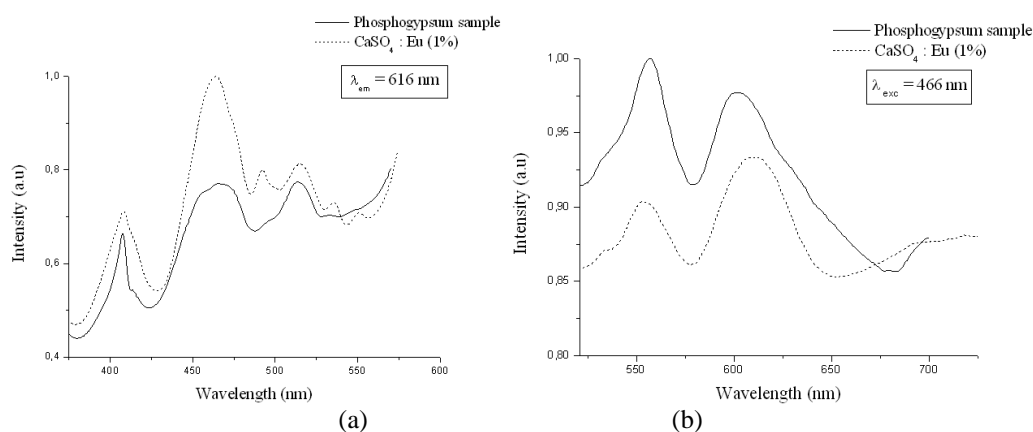


Figure.3. Superposition of a) excitation spectra at $\lambda_{\text{em}} = 616$ nm and b) Emission spectra at $\lambda_{\text{exc}} = 466$ nm of the raw phosphogypsum sample and the synthetic $\text{CaSO}_4:\text{Eu}$ (1%).

Europium emission lifetime in the synthetic $\text{CaSO}_4:\text{Eu}$ and the PG

Measures of a lifetime (τ) europium emission at 615 nm (characteristic of the transition $^5\text{D}_0 - ^7\text{F}_2$) were performed for the synthetic $\text{CaSO}_4:\text{Eu}$ (1%) and the phosphogypsum sample. The obtained curves, depicted in figures 4 and 5, show that the 615 nm line has different delay time for both samples: 0.9 ms for the synthetic gypsum doped with europium and 0.11 ms for the Tunisian phosphogypsum. Since lifetime emission of a luminophore is influenced by its environment²³, this difference can be explained by the presence of water molecules as well as various impurities in the phosphogypsum contributing thus to transfer energy phenomena and decreasing its europium emission lifetime in comparison with that of the synthetic $\text{CaSO}_4:\text{Eu}$ (1%).

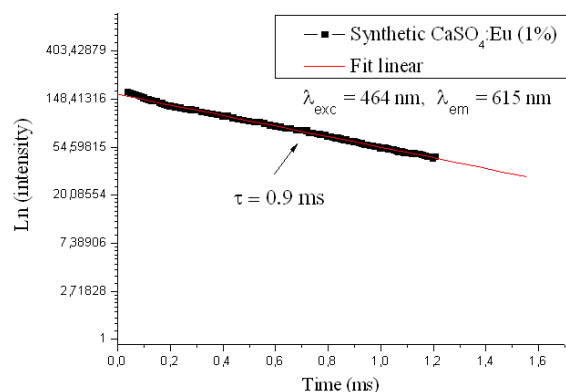


Figure.4. The curve of Eu^{3+} lifetime emission at 615 nm for the synthetic $\text{CaSO}_4:\text{Eu}$ (1%).

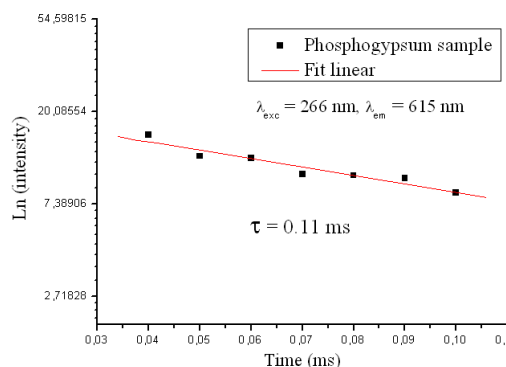


Figure.5. The curve of Eu^{3+} lifetime emission at 615 nm for the phosphogypsum sample.

The values of a determined lifetime are similar to those of the literature. M. Gaft et al.²⁴ and R. Reisfeld et al.²⁵ showed that the emission of trivalent europium at around 618 nm can take up to 1.6 - 1.9 ms depending on the mineral type.

The lifetime of Eu^{2+} emission (transition $4f^65d \rightarrow 4f^7$) in the synthesized gypsum could not be measured because of its rapidity, which is in the vicinity of 600 - 800 ns²⁶.

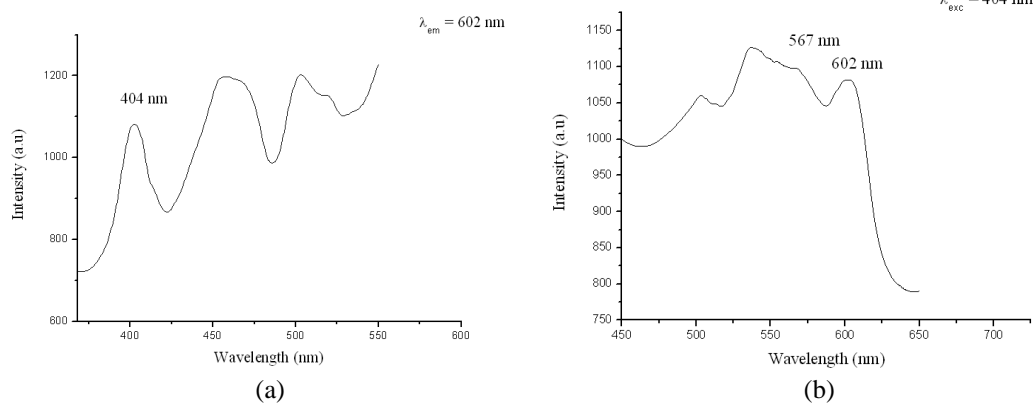


Figure.6. a) Excitation spectrum at $\lambda_{em}=602$ nm and b) Emission spectrum at $\lambda_{exc}=404$ nm of the raw phosphogypsum sample showing the Sm^{3+} emissions.

Samarium emission lifetime

Although the Sm^{3+} emission lifetime at 607 nm is around 2 - 2.5 ms (near to that of Eu^{3+} at 616 nm)^{24,25} the measurements made on the phosphogypsum gave a quick response exceeding the detection limit of the apparatus. The presence of impurities and other rare earth elements, responsible for energy transfer phenomena, can be the cause of the rapid response of the samarium luminescence in the phosphogypsum.

Cerium luminescence

Excitations of the raw phosphogypsum at energetic wavelengths (around 260 nm) did not allow the observation of the characteristic emissions of the cerium ion (Fig.7). The band obtained at 342 nm corresponds to a matrix emission²². Generally, and in a gypsum sample, Ce^{3+} emissions are located at about 305 nm and 325 nm as a doublet^{11,12,29,30}.

Samarium luminescence

In the rest of this work we relied on the literature for the identification of rare earth emissions. In fact, once the characteristic europium emissions in the phosphogypsum sample were identified, selective excitations of this latter at characteristic samarium transitions, determined from the literature, were performed.

Samarium emission in the phosphogypsum

The excitation spectrum at $\lambda_{em} = 602$ nm of the Tunisian phosphogypsum (see Fig.6 (a)) confirms that the selective wavelength of the $^4G_{5/2}-^6H_{7/2}$ transition is situated at 404 nm. Figure 6 (b), representing the emission spectrum of the sample after its excitation at 404 nm, showed the characteristic bands of the trivalent samarium at around 567 nm and 602 nm. These bands correspond respectively to $^4G_{5/2}-^6H_{5/2}$ and $^4G_{5/2}-^6H_{7/2}$ transitions of Sm^{3+} ^{19,27,28}.

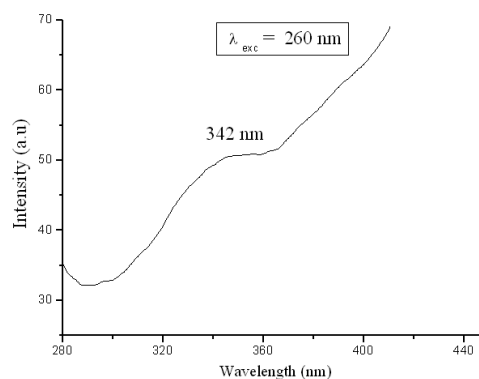


Figure.7. The emission spectrum of the raw Tunisian phosphogypsum after excitation at 260 nm.

Calcination of the studied sample at 900°C has improved the photoluminescence response and allowed to visualize more clearly cerium emissions around 305 nm and 326 nm after excitation at 254 nm (see Figure.8). These luminescence bands

correspond to the lowest lying 5d level of the ${}^2F_{5/2}$ and the ${}^2F_{7/2}$ level of the 4f state of Ce^{3+} ion¹². This PL response improvement is quite related to the

crystallinity change of the sample after its thermal treatment (from dihydrated to anhydrite).

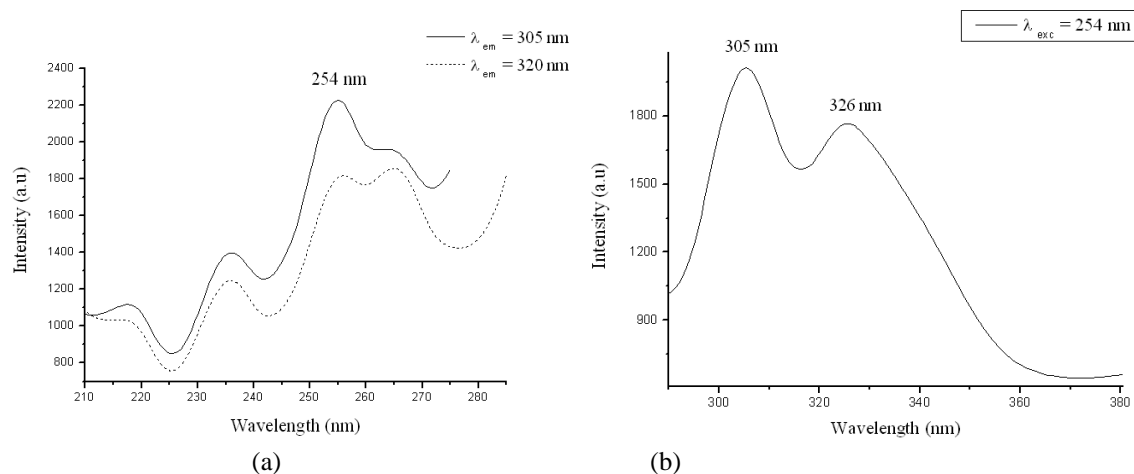


Figure.8. a) Excitation spectra at $\lambda_{em}= 305$ and 320 nm and b) Emission spectrum at $\lambda_{exc}= 254$ nm of the calcined phosphogypsum showing Ce^{3+} emissions.

It is known that the lifetime for cerium emission in minerals is so rapid (near 20-30 ns)^{24,25}, that it could not be determined by the device available in the laboratory.

Conclusion

This study showed that photoluminescence technique can be used as a complementary method for the detection of rare earth elements present in a phosphogypsum by-product of the acid phosphoric industry. ICP-MS analysis of the studied sample proved the presence of such elements with a total content of 350.21 ppm.

Selective excitations of the phosphogypsum (at 466 nm and 404 nm) allowed the observation of the characteristic emissions of Eu^{3+} around 556 nm and 603 nm (transitions ${}^5D_1 - {}^7F_2$ and ${}^5D_0 - {}^7F_2$ respectively) and the characteristic emissions of Sm^{3+} at 567 nm and 602 nm (transitions ${}^4G_{5/2} - {}^6H_{5/2}$ and ${}^4G_{5/2} - {}^6H_{7/2}$ respectively). Whereas, cerium emissions (Ce^{3+}) were observed only after thermal treatment of the phosphogypsum sample at 900°C. The characteristic bands of this element, obtained after excitation of the sample at 254 nm, are located at 305 nm and 326 nm as a doublet (5d-4f transitions).

A lifetime of Eu^{3+} emission at 615 nm in the phosphogypsum (0.11 ms) was lower in comparison with that in the synthetic $CaSO_4: Eu$ (0.9 ms). This is due to energy transfer phenomena with the various impurities present in the phosphogypsum. This effect of impurities presence was also observed for the Sm^{3+} emission at 607 nm. This emission (generally near to that of europium) was so fast that the apparatus could not measure it.

References

- 1- D. Van Der Voort, G. Blasse, G.J. Witkamp, G.M. Van Rosmalen, L.H. Brixner, *Materials Chemistry and Physics*, **1989**, 24, 175-187.
- 2- F. Pereira, *Thesis*, Saint-Etienne, Ecole Nationale Supérieure des Mines et Université Jean Monnet, **2003**.
- 3- V. Bourcier, *Thesis*, Saint-Etienne, Ecole Nationale Supérieure des Mines, **2007**.
- 4- F. Habashi, *Journal of Chemical Technology and Biotechnology*, **1985**, 35 A, 5 - 14.
- 5- G. Tyler, *Plant and Soil*, **2004**, 267, 191-206.
- 6- G. Le Flem, C. Parent, C. Fouassier, *Journal of the Less-Common Metals*, **1983**, 93, 383-388.
- 7- J. Ballato, J. S. Lewis III, P. Holloway, *Materials Research Bulletin*, **1999**, 9, 51-56.
- 8- R.J. Xie, M. Mitomo, K. Uheda, F.F. Xu, Y. Akimune, *Journal of the American Ceramic Society*, **2002**, 85, 1229-1234.
- 9- J. Lindmayer, P. Goldsmith, C. Wrigley, *Laser Focus World*, **1989**, 119.
- 10- A. Winnacker, R.M. Shelby, R.M. Macfarlane, *Optics Letters*, **1985**, 10, 350-352.
- 11- A.M. Muke, P.L. Muthal, S.M. Dhopte, S.V. Moharil, *Journal of Luminescence*, **2012**, 132, 342-344.
- 12- D. Van Der Voort, G. Blasse, *Journal of Solid State Chemistry*, **1990**, 87, 350-359.
- 13- S.M. Dhopte, P.L. Muthal, V.K. Kondawar and S.N. Moharil, *Journal of Luminescence*, **1991**, 50, 187-195.
- 14- E. Cantelar, G. Lifante, T. Calderon, R. Melendrez, A. Millan, M.A. Alvarez, M. Barboza-Flores, *Journal of Alloys and Compounds*, **2001**, 323-324, 851-854.

- 15- A. Mastandrea, D. Barca, A. Guido, F. Tosti, F. Russo, *Carbonates Evaporites*, **2010**, 25, 133-143.
- 16- M. Marques Fernandes, M. Schmidt, T. Stumpf, C. Walther, D. Bosbach, R. Klenze, Th. Fanghänel, *Journal of Colloid and Interface Science*, **2008**, 321, 323-331.
- 17- S.V. Godbole, J.S. Nagpal, A.G. Page, *Radiation Measurements*, **2000**, 32, 343-348.
- 18- G. Blasse, G. P. M. Van Den Heuvel, J. Stegenga, *Journal of Solid State Chemistry*, **1976**, 17, 439 - 441.
- 19- S.A. Mohitkar, G. Kalpana, K. Vidyasagar, *Journal of Solid State Chemistry*, **2011**, 184, 735-740.
- 20- A. Moadhen, H. Elhouichet, M. Oueslati, M. Férid, *Journal of Luminescence*, **2002**, 99, 13-17.
- 21- R.D. Shannon, *Acta Crystallographica*, **1976**, A32, 751.
- 22- I. Hammam, K. Horchani-Naifer, M. Férid, *Studies in Chemical Process Technology*, **2013**, 1, 30 - 36.
- 23- G. Plancque, V. Moulin, P. Toulhoat, C. Moulin, *Analytica Chimica Acta*, **2003**, 478, 11-22.
- 24- M. Gaft, R. Reisfeld, G. Panczer, Ph. Blank, G. Boulon, *Spectrochimica Acta. Part A*, **1998**, 54, 2163-2175.
- 25- R. Reisfeld, M. Gaft, G. Boulon, C. Panczer, C.K. Jorgensen, *Journal of Luminescence*, **1996**, 69, 343-353.
- 26- M. Gaft, *Water Science and Technology*, **1993**, 27, 547.
- 27- A. Bao-Li, G. Meng-Lian, L. Ming-Xing, Z. Ji-Ming, *Journal of Molecular Structure*, **2004**, 687, 1-6.
- 28- J. Sun, R. Sun, H. Du, *Journal of Alloys and Compounds*, **2012**, 516, 201-206.
- 29- A.P. Vink, E. Van Der Kolk, P. Dorenbos, C.W.E. Van Eijk, *Optics Communications*, **2002**, 210, 277-284.
- 30- M. Zahedifar, M. Mehrabi, *Nuclear Instruments & Methods*, **2010**, B 268, 3517-3522.