ESRF	**Experiment title:** **Lanthanide Silicates Exhibiting Unusual Photoluminescent Properties**	**Experiment number**: CH-2832
Beamline: ID11	**Date of experiment**: from: 30 – Nov. – 2009 to: 04 – Dec. – 2009	**Date of report**: 23 – Feb. – 2012 *Received at ESRF:*
Shifts: 9	**Local contact(s)**: Dr. Gavin Vaughan (E-mail: vaughan@esrf.fr)	

Names and affiliations of applicants (* indicates experimentalists):

Professor João Rocha

Dr. Filipe A. Almeida Paz *

Dr. Duarte Ananias *

Dr. Luís Cunha-Silva *

Affiliation:
University of Aveiro, CICECO, Department of Chemistry, 3810-193 Aveiro, Portugal.

Introduction and General Aim of the Experiment:

Over the last decade or so our research group has been leading the worldwide research focused at the engineering of optical metallic centres (in particular lanthanide cations) into silicate matrices with the aim to produce inorganic functional materials, many of which exhibit structural properties similar to those found in zeo-type compounds.[1-17] A few years ago we discovered a new family of chiral compounds, formulated as $Na_3[(Y,Ln)Si_3O_9]\cdot 3H_2O$ (where Ln^{3+} could be Eu^{3+}, Tb^{3+}, Er^{3+} or Ce^{3+}), which strongly resembles a zeolite material: $(Si_3O_9)_\infty$ chains, running along the [100] direction, are interconnected by lanthanide cations leading to a three-dimensional porous framework having 8-ring channel (*ca.* 2.0×4.0 Å cross-section) which host Na^+ and hydrogen-bonded water molecules. Remarkably, for the Eu^{3+}-containing material we found that Eu^{3+} photoluminescence spectroscopy was able to identify, and possibly quantify, enantiomeric domains in the chiral frameworks by using unpolarised light excitation and in the absence of an external magnetic field.[6] At the time we postulated that when the material was irradiated with UV light some structural changes could occur; these modifications, due to their structural importance, could then be visible from X-ray studies at very low temperature.

The aim of this proposal was to collect single-crystal X-ray diffraction data for $Na_3[(Y_{0.70}Eu_{0.30})Si_3O_9]\cdot 3H_2O$ at ambient, 100K and another lower temperature, with and without UV irradiation, and investigate if any structural change was indeed noticeable.

Results and Discussion:

$Na_3[(Y_{0.70}Eu_{0.30})Si_3O_9]\cdot3H_2O$

A significant portion of the first day of the experiment was dedicated to fully explain the idea, the general aim of the proposal and which were our personal and specific objectives to our local contact, Dr. Gavin Vaughan.

Our portable UV excitation source (Figure 1) was mounted inside the experimental hutch, close to the location were the crystal was going to be placed, and some tests were performed to antecipate any collision with the accessories already in place at the ID11 experimental hutch.

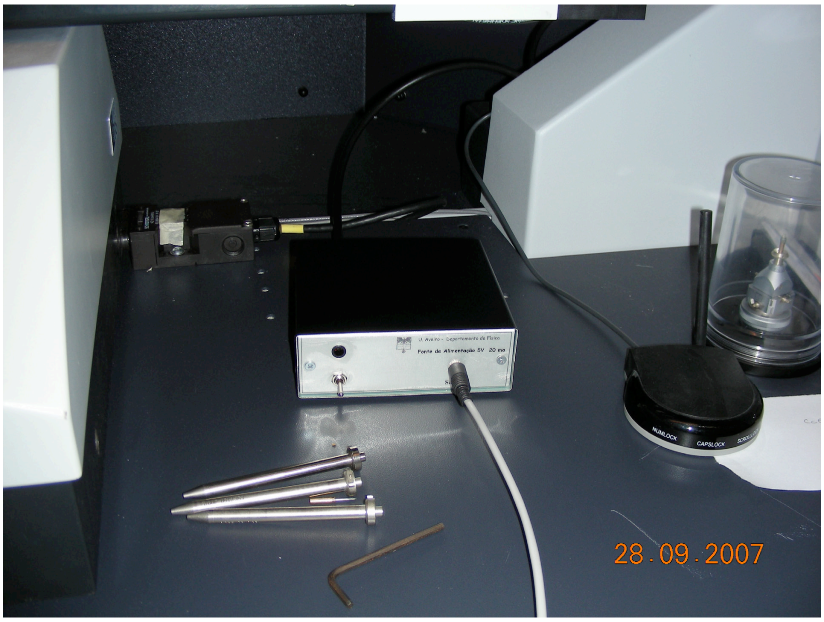


Figure 1. In-house portable apparatus for a constant UV excitation.

Experiments on a suitable single-crystal of $Na_3[(Y_{0.70}Eu_{0.30})Si_3O_9]\cdot3H_2O$ started at the end of the afternoon of the first day and covered a wide range of conditions: ambient temperature, 100K and 18K; for all temperatures a full data set was collected with and without UV irradiation; for 18K with UV irradiation, two full data sets were collected. *Please note*: some experiments had to be repeated with and without attenuator, in particular at low temperature, due to the very strong intensity of some reflections. Table 1 summarizes the most relevant results obtained for the same crystal at different experimental conditions (only the head of the INS SHELX file is presented for clarity).

From the collected data sets (only 7 are shown) we did not find any evidence for our initial assumptions: independently of the employed conditions, the irradiation of the material with UV light did not produce a noticeable structural change which could be observed *in situ* by single-crystal X-ray diffraction. In fact all data sets could be equally solved and refined in the chiral $P2_12_12_1$ space group with very similar *R*-factors.

Table 1. Unit cell parameters for the $Na_3[(Y_{0.70}Eu_{0.30})Si_3O_9]\cdot 3H_2O$ material collected at different experimental conditions (single-crystal data).

Ambient temperature

```
TITL RT in P2(1)2(1)2(1)
CELL 0.31849   7.0084  11.7147  13.4516  90.000  90.000  90.000
ZERR    4.00   0.0003   0.0005   0.0006   0.000   0.000   0.000
```

100K

```
TITL 100K in P2(1)2(1)2(1)
CELL 0.31849   7.0291  11.7452  13.5141  90.000  90.000  90.000
ZERR    4.00   0.0001   0.0002   0.0003   0.000   0.000   0.000
```

100K with UV irradiation

```
TITL 100K_UV in P2(1)2(1)2(1)
CELL 0.31849   7.0296  11.7453  13.5122  90.000  90.000  90.000
ZERR    4.00   0.0003   0.0005   0.0006   0.000   0.000   0.000
```

18K (no attenuator)

```
TITL 18K in P2(1)2(1)2(1)
CELL 0.31849   7.0073  11.7126  13.4752  90.000  90.000  90.000
ZERR    4.00   0.0003   0.0005   0.0007   0.000   0.000   0.000
```

18K (with attenuator)

```
TITL 18K_att in P2(1)2(1)2(1)
CELL 0.31849   7.0073  11.7126  13.4752  90.000  90.000  90.000
ZERR    4.00   0.0003   0.0005   0.0007   0.000   0.000   0.000
```

18K (no attenuator) with UV irradiation

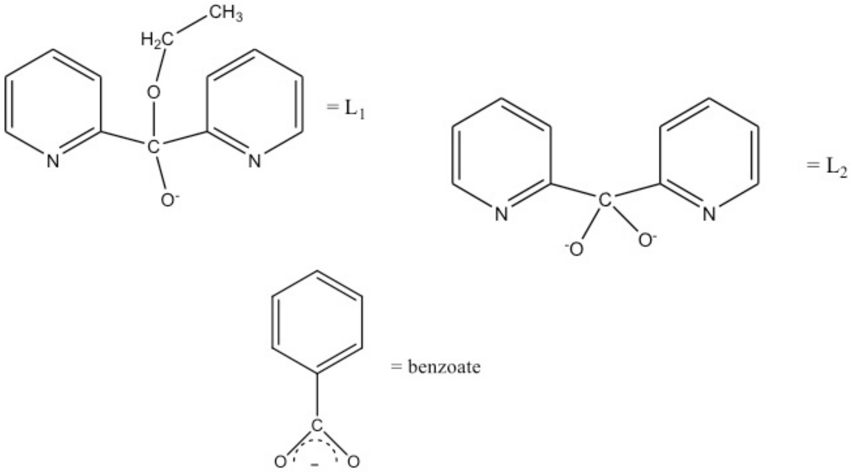
```
TITL 18K_UV in P2(1)2(1)2(1)
CELL 0.31849   7.0258  11.7386  13.4763  90.000  90.000  90.000
ZERR    4.00   0.0100   0.0118   0.0226   0.000   0.000   0.000
```

18K (no attenuator) with UV irradiation (2nd run)

```
TITL 18K_UVb in P2(1)2(1)2(1)
CELL 0.31849   6.9683  11.6239  13.3798  90.000  90.000  90.000
ZERR    4.00   0.0005   0.0010   0.0011   0.000   0.000   0.000
```

$[Mn_{20}O_{10}(PhCOO)_2(L1)_2(L2)_{18}]\cdot 2EtO\cdot MeOH$

In the remaining allocated time for the experiment we were also able to collect a full data set for the high nuclearity cluster of manganese depicted in Figure 2 (see Scheme 1 for the chemical structure of the ligands). We are still waiting to publish this result due to a combination of several factors, with the most relevant being the need to scale-up the synthesis so the magnetic properties could be studied in detail.



Scheme 1. Organic ligands present in the high-nuclearity cluster $[Mn_{20}O_{10}(PhCOO)_2(L1)_2(L2)_{18}]$.

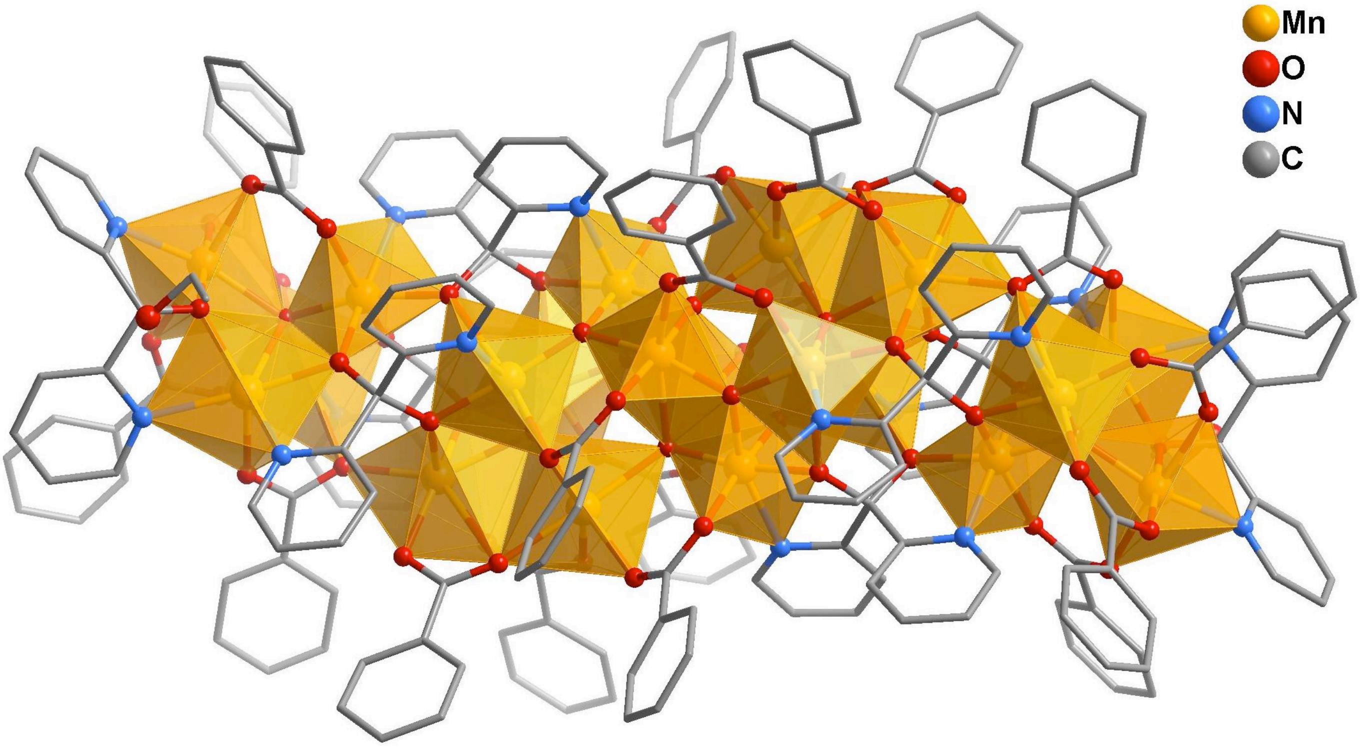


Figure 2. Schematic representation of the high-nuclearity cluster $[Mn_{20}O_{10}(PhCOO)_2(\mathit{L1})_2(\mathit{L2})_{18}]$.

Conclusions:

In summary, we believe that the time allocated for this experiment, alongside with the good interaction with Dr Gavin Vaughan, who was very helpful and contributed very actively giving suggestions for the experiments, were sufficient guaranteeing the collection of the data sets needed to reach the aforementioned conclusions.

Even though we did not observe the structural change which was much anticipated before the experiment, we also do not believe that this occurred due to any limitation of the apparatus at the ID11 beam line or to any lack of support from our local contact: all efforts were, indeed, taken so to exhaustively investigate the system to see if any structural change was noticeable upon UV irradiation of the crystals. We are, thus, led to the overall conclusion that the effect is indeed not structurally visible, at least when using X-ray diffraction to monitor the changes.

We anticipate that one publication may arise from this experiment in the near future reporting the crystal structure of the high-nuclearity cluster $[Mn_{20}O_{10}(PhCOO)_2(\mathit{L1})_2(\mathit{L2})_{18}]$, for which a full data set was collected during our visit to the ESRF under the present project.

Acknowledgements

We are very grateful to Dr Gavin Vaughan for assistance with data collection and treatment, and also for fruitful discussions. We also would like to thank Fundação para a Ciência e a Tecnologia (FCT, Portugal), FEDER and COMPETE for financial support.

References

[1] D. Ananias, M. Kostova, F. A. A. Paz, A. N. C. Neto, R. T. De Moura, O. L. Malta, L. D. Carlos, J. Rocha, *J. Am. Chem. Soc.* **2009**, *131*, 8620-8626.

[2] C. M. Kowalchuk, F. A. A. Paz, D. Ananias, P. Pattison, L. D. Carlos, J. Rocha, *Chem.-Eur. J.* **2008**, *14*, 8157-8168.

[3] M. H. Kostova, D. Ananias, L. D. Carlos, J. Rocha, *J. Alloy. Compd.* **2008**, *451*, 624-626.

[4] M. H. Kostova, D. Ananias, F. A. A. Paz, A. Ferreira, J. Rocha, L. D. Carlos, *J. Phys. Chem. B* **2007**, *111*, 3576-3582.

[5] M. H. Kostova, R. A. S. Ferreira, D. Ananias, L. D. Carlos, J. Rocha, *J. Phys. Chem. B* **2006**, *110*, 15312-15316.

[6] D. Ananias, F. A. A. Paz, L. D. Carlos, C. Geraldes, J. Rocha, *Angew. Chem.-Int. Edit.* **2006**, *45*, 7938-7942.

[7] D. Ananias, L. D. Carlos, J. Rocha, *Opt. Mater.* **2006**, *28*, 582-586.

[8] G. A. Pereira, D. Ananias, J. Rocha, V. S. Amaral, R. N. Muller, L. V. Elst, E. Toth, J. A. Peters, C. Geraldes, *J. Mater. Chem.* **2005**, *15*, 3832-3837.

[9] J. Rocha, L. D. Carlos, F. A. A. Paz, D. Ananias, J. Klinowski, in *Recent Advances in the Science and Technology of Zeolites and Related Materials, Pts a - C, Vol. 154* (Eds.: E. VanSteen, M. Claeys, L. H. Callanan), Elsevier Science Bv, Amsterdam, **2004**, pp. 3028-3035.

[10] J. Rocha, L. D. Carlos, A. Ferreira, J. Rainho, D. Ananias, Z. Lin, in *Advanced Materials Forum Ii, Vol. 455-456* (Eds.: R. Martins, E. Fortunato, I. Ferreira, C. Dias), Trans Tech Publications Ltd, Zurich-Uetikon, **2004**, pp. 527-531.

[11] J. P. Rainho, D. Ananias, Z. Lin, A. Ferreira, L. D. Carlos, J. Rocha, *J. Alloy. Compd.* **2004**, *374*, 185-189.

[12] D. Ananias, J. P. Rainho, A. Ferreira, J. Rocha, L. D. Carlos, *J. Alloy. Compd.* **2004**, *374*, 219-222.

[13] D. Ananias, M. Kostova, F. A. A. Paz, A. Ferreira, L. D. Carlos, J. Klinowski, J. Rocha, *J. Am. Chem. Soc.* **2004**, *126*, 10410-10417.

[14] A. Ferreira, D. Ananias, L. D. Carlos, C. M. Morais, J. Rocha, *J. Am. Chem. Soc.* **2003**, *125*, 14573-14579.

[15] D. Ananias, A. Ferreira, L. D. Carlos, J. Rocha, *Adv. Mater.* **2003**, *15*, 980-+.

[16] D. Ananias, J. P. Rainho, A. Ferreira, M. Lopes, C. M. Morais, J. Rocha, L. D. Carlos, *Chem. Mat.* **2002**, *14*, 1767-1772.

[17] D. Ananias, A. Ferreira, J. Rocha, P. Ferreira, J. P. Rainho, C. Morais, L. D. Carlos, *J. Am. Chem. Soc.* **2001**, *123*, 5735-5742.