



	Experiment title: New Rare-Earth Heteropolyhedra Luminescent Materials	Experiment number: CH-2253
Beamline: BM01b	Date of experiment: from: 28 – Sept. – 2006 to: 02 – October – 2006	Date of report: 29 – Aug. – 2007
Shifts: 12	Local contact(s): Dr. Wouter Van Beek (E-mail: wouter@esrf.fr)	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): <p style="text-align: center;">Professor João Rocha ^[a] Dr. Filipe A. Almeida Paz ^[a] * Dr. Artur Ferreira ^[b] * Dr. Luís Cunha-Silva ^[a] *</p> <p><i>Affiliations:</i> ^[a] University of Aveiro, CICECO, Department of Chemistry, 3810-193 Aveiro, Portugal. ^[b] University of Aveiro, CICECO, ESTGA, 3810-193 Aveiro, Portugal</p>		

Report:

Over the last decade or so our group has been particularly active in the hydrothermal synthesis (under mild conditions) of novel functional materials containing lanthanide centers, in particularly microporous heteropolyhedra rare-earth silicates (MHRESs) [1-11] and, more recently, rare-earth-organic frameworks (REOFs) with highly flexible organic ligands containing one or more phosphonic acid group(s) [12,13]. Because these functional materials are, in most of the cases, isolated directly from the autoclave contents as microcrystalline powders or as extremely small single-crystals (thus unsuitable for conventional single-crystal X-ray diffraction studies), the structural intricacies of some families of compounds have eluded us for some time. Even though powder X-ray diffraction patterns collected using commercial instruments can in most of the cases provide useful information concerning novelty and phase purity (from preliminary indexing of the patterns), these also suffer from severe lack of angular resolution and are affected by strong preferential orientation. When combined, these two factors significantly decrease the possibility of solving and refining the structure of MHRESs and REOFs using *ab initio* methods.

The aim of this proposal was to collect high-resolution powder X-ray diffraction data for: (1) a series of isostructural MHRESs (with different lanthanides) belonging to the AV-21 family, for which the exact structural details are still unknown to date; (2) a series of REOFs containing nitrilotris(methylphosphonic acid) (H₆NMP). Preliminary studies showed that the collected powder patterns for all these compounds using a conventional instrument were severely affected by strong preferential orientation. It was expected that the high brilliance of the synchrotron source in combination with the increased line resolution would allow us to, finally, solve and refine their crystal structures.

Microporous Heteropolyhedra Rare-Earth Silicates (MHRESs)

The AV-21 system was reported by our research group a few years ago [11]. However, that initial full crystallographic description was significantly affected by a series of errors which could not be overcome by using conventional single-crystal X-ray diffraction. In particular, even though a reliable indexing could be usually possible for any synthesized crystal, single-crystal data collected for many different samples obtained from different batches and under different experimental set ups (e.g., different instruments) systematically failed to provide reliable information on the systematic absences in order to fully determine the space group. Due to the high crystallinity of the samples the scientific contact for this experiment, Dr. Wouter Van Beek put us in contact with Dr. Philip Pattison who collected micro-crystal data (BM01a beam line), at the low temperature of 100(2) K, for the samarium-containing sample: $\text{Na}_4(\text{Na}_{1.29}\text{Sm}_{0.24})[\text{Sm}_2\text{Si}_{12}\text{O}_{30}]\cdot 4.88\text{H}_2\text{O}$ (AV-21-Sm). This new set of collected reflections allowed us to unequivocally determine the structure of AV-21-Sm in the orthorhombic $Pmna$ space group (Figure 1): $\text{Na}_{5.29}\text{O}_{34.88}\text{Si}_{12}\text{Sm}_{2.24}$, $Z = 1$, $a = 7.53 \text{ \AA}$, $b = 7.05 \text{ \AA}$, $c = 14.99 \text{ \AA}$, $V = 795.767(16) \text{ \AA}^3$; of a total of 3371 reflections collected, 683 were independent ($R_{\text{int}} = 0.0557$); final $R1 = 0.0517$ [$I > 2\sigma(I)$] and $wR2 = 0.1399$ (all data). Micro-crystal data were also collected for the gadolinium and one mixed terbium/europium sample, which proved to be isostructural with AV-21-Sm (Figure 1). This detailed structural information in conjunction with the photophysical properties are now being systematised in the form a manuscript which will be submitted to a highly reputed international journal in this area of research.

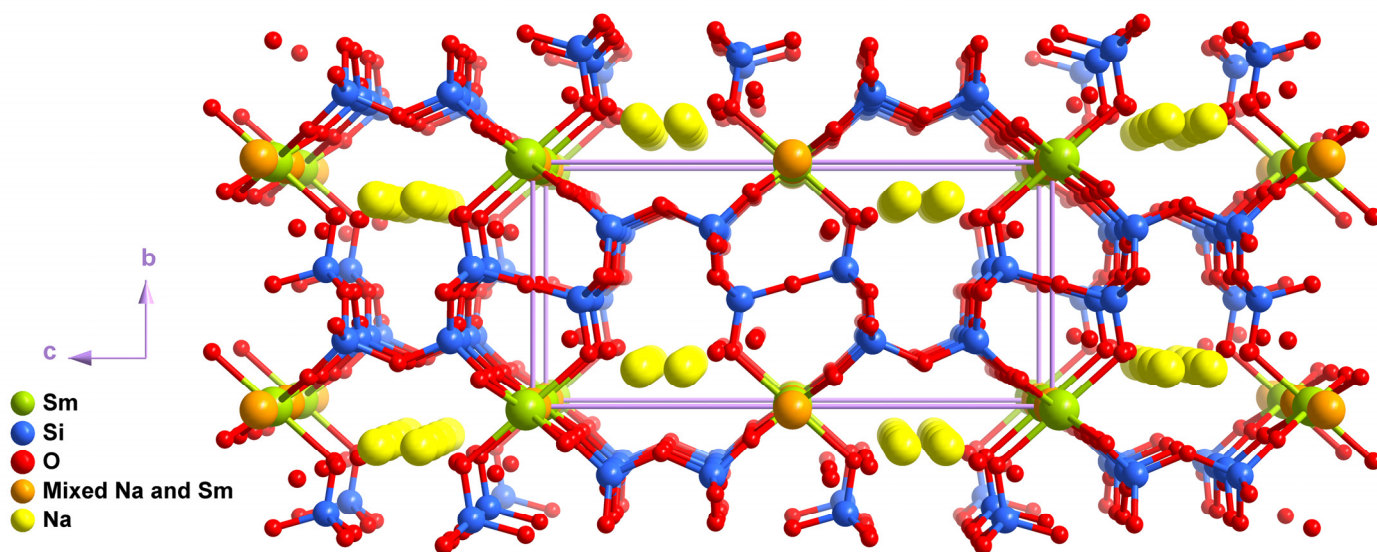


Figure 1. Crystal packing of $\text{Na}_4(\text{Na}_{1.29}\text{Sm}_{0.24})[\text{Sm}_2\text{Si}_{12}\text{O}_{30}]\cdot 4.88\text{H}_2\text{O}$ (AV-21-Sm) viewed in perspective along the [100] crystallographic direction.

Rare-Earth-Organic Frameworks (REOFs)

The hydrothermal reaction between H_6NMP and lanthanide centres leads to the isolation as microcrystalline powders of a series of REOFs formulated as $[\text{Ln}(\text{H}_3\text{NMP})]\cdot 1.5(\text{H}_2\text{O})$ (where $\text{Ln}^{3+} = \text{La}^{3+}$, Pr^{3+} , Nd^{3+} , Sm^{3+} and Eu^{3+}) (Figure 2). This family of compound exhibits photoluminescence properties and reversible removal of the inter-layer water molecules. The anisotropic lath-like crystal morphology of these materials prevented crystal solution from conventional powder pattern. High-resolution PXRD data for $[\text{Pr}(\text{H}_3\text{NMP})]\cdot 1.5(\text{H}_2\text{O})$ was collected at the BM01b beam line ($\lambda = 0.50018(1) \text{ \AA}$; Figure 2 – bottom) which,

when used in tandem with data derived from high-resolution solid-state NMR studies, allowed the unequivocal elucidation of the fine structural details of this family of functional materials: $a = 27.5001(4) \text{ \AA}$, $b = 11.99777(18) \text{ \AA}$, $c = 7.25373(11) \text{ \AA}$, $V = 2393.30(6) \text{ \AA}^3$, space group $Pbcn$, zero shift of $-0.0026(2)^\circ$, $R_p = 7.81\%$, $R_{wp} = 10.49\%$, $R_{exp} = 8.23\%$, $\chi^2 = 1.62$, $R_{Bragg} = 5.64\%$. The full structural details and photophysical properties of this family of compounds has been recently published in *Chemistry of Materials* [12].

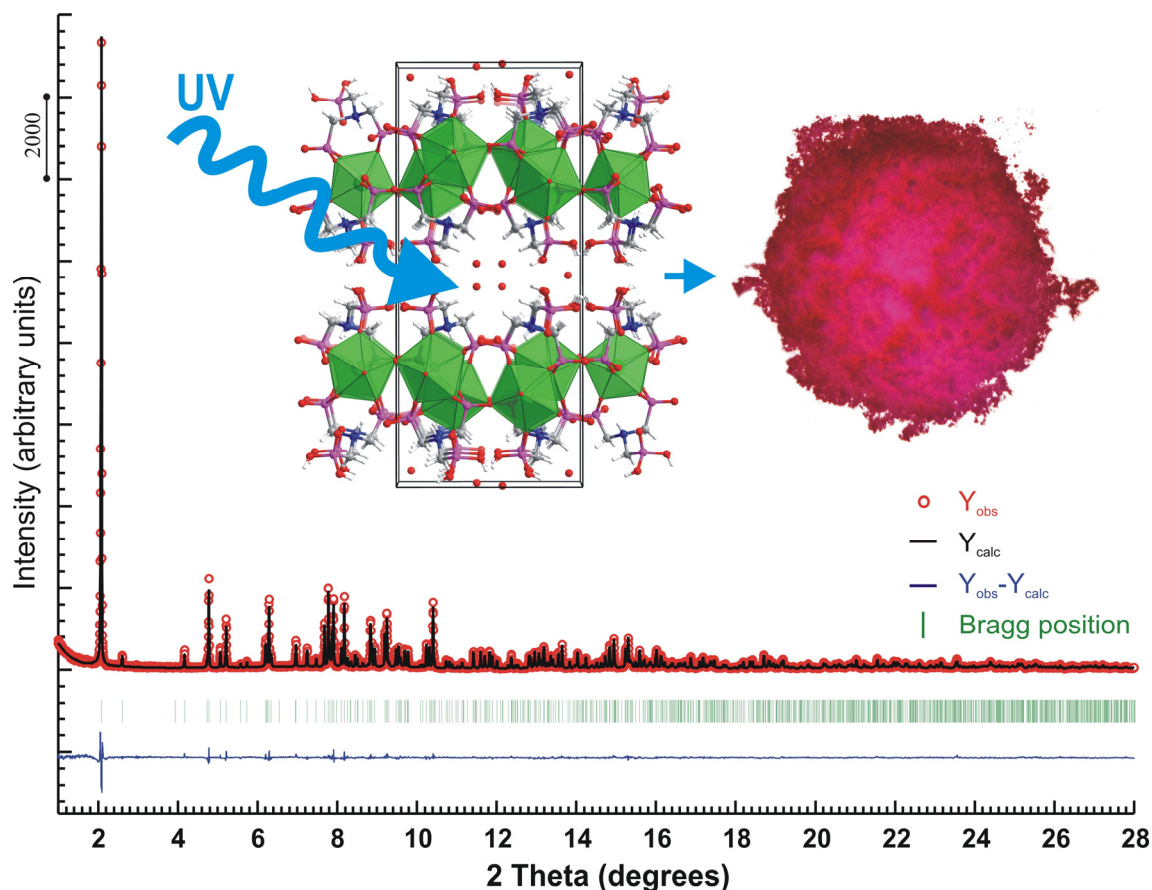


Figure 2. Final Rietveld plot and crystal packing of $[\text{Pr}(\text{H}_3\text{NMP})]\cdot 1.5(\text{H}_2\text{O})$. Photoluminescence (in the visible region) of the isostructural material with Eu^{3+} while under ultraviolet irradiation.

During the allocated time for this experiment, high-resolution data was also collected for a novel organic-inorganic hybrid material which was formulated *a posteriori* as $[\text{Ge}_3\text{O}_6(\text{DCH-99})]\cdot \text{H}_2\text{O}$ [where DCH-99 stands for 1,2-diaminocyclohexane]. The powder pattern [$\lambda = 0.50018(1) \text{ \AA}$] was unequivocally indexed using DICVOL04 [$a = 5.32421(5) \text{ \AA}$, $b = 7.43224(6) \text{ \AA}$, $c = 15.09971(13) \text{ \AA}$, $V = 597.508(9) \text{ \AA}^3$, space group $P2_12_12_1$] with high figures-of-merit [$M(25) = 191.2$ and $F(25) = 1276.0$; zero shift of -0.0076°], and ultimately allowed a sensible full crystal solution and refinement using Fullprof.2k (Figure 3): independent reflections = 1071, global refined parameters = 1, profile refined parameters = 11, intensity-dependent refined parameters = 49, $R_p = 9.96\%$, $R_{wp} = 13.52\%$, $R_{exp} = 6.06\%$, $\chi^2 = 4.97$, $R_{Bragg} = 5.33\%$ and $R_F = 7.99\%$. This information is now being systematised in the form a manuscript which will be submitted to a highly reputed international journal in this area of research.

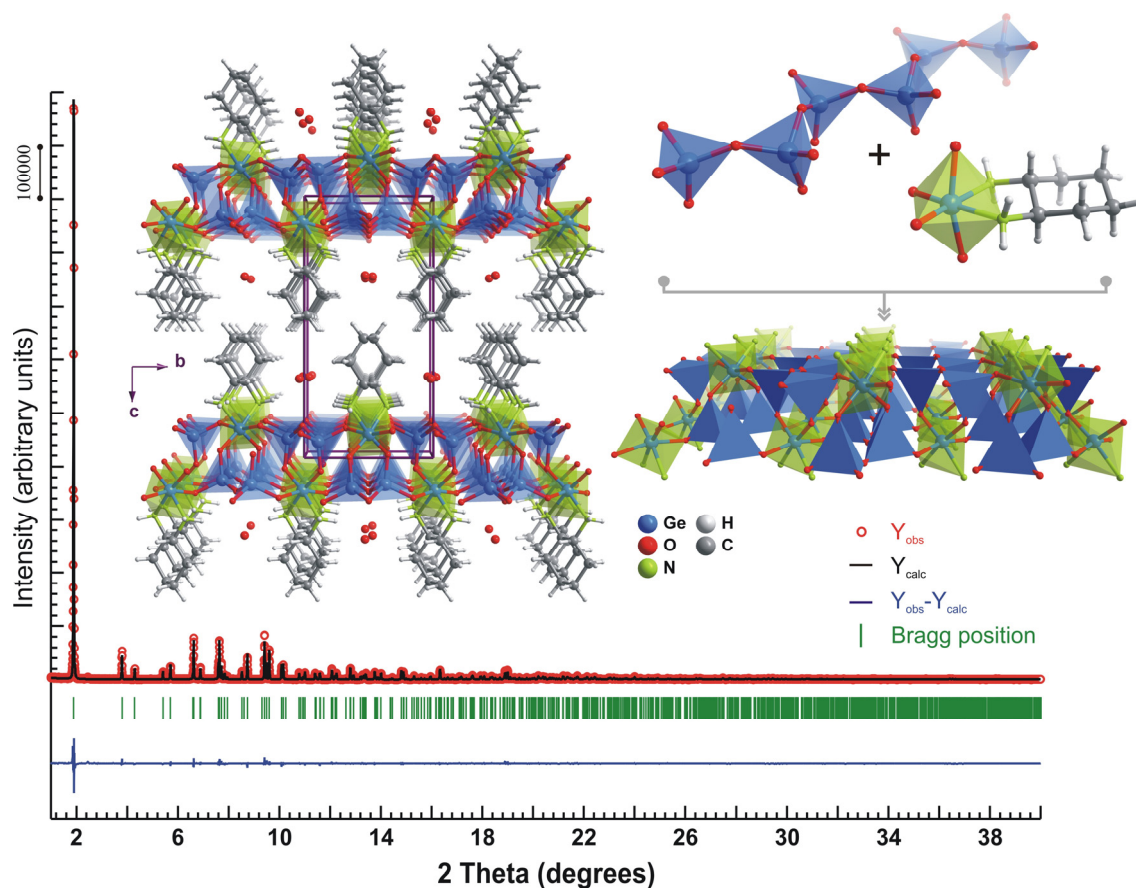


Figure 3. Final Rietveld plot and crystal packing of $[\text{Ge}_3\text{O}_6(\text{DCH-99})]\cdot\text{H}_2\text{O}$ [where DCH-99 stands for 1,2-diaminocyclohexane].

Conclusions

In summary, we believe that the time allocated for this experiment alongside with the good interaction with Drs Van Beek and Pattison, were remarkable and culminated in the acquisition of excellent high-resolution data which ultimately allowed us to solve the structures for the three families of compounds described above. In particular, from our personal experience, even though a good high-resolution powder pattern for a novel REOF collected at BM01b needs at least 8-10 hours of beam time, this beam line also has the great advantage of not destroying the samples due to radiation damage (an experimental fact registered recently by some of the experimentalists listed in the header at beam line ID31). This feature renders BM01b the ideal beam line for most of the work on organic-inorganic hybrid materials synthesized and studied in our laboratories. Future access to this facility will most certainly increasing the possibility of producing in the future results at least as good and with the same scientific impact as those described above.

Acknowledgements

We gratefully acknowledge Dr. Wouter Van Beek and Dr. Philip Pattison for assistance with data collection at the BM01b and BM01a beam lines, respectively. We also would like to thank the Portuguese Foundation for Science and Technology for financial support under the project number POCI/QUI/58377/2004 supported by FEDER.

References

- [1] Rocha, J.; Lin, Z. In *Micro- and Mesoporous Mineral Phases*; Mineralogical Soc America: Washington, 2005; 57; pp. 173-201.
- [2] Ananias, D.; Rainho, J. P.; Ferreira, A.; Rocha, J.; Carlos, L. D. *J. Alloy. Compd.* **2004**, *374*, 219-222.
- [3] Ananias, D.; Kostova, M.; Paz, F. A. A.; Ferreira, A.; Carlos, L. D.; Klinowski, J.; Rocha, J. *J. Am. Chem. Soc.* **2004**, *126*, 10410-10417.
- [4] Ferreira, A.; Ananias, D.; Carlos, L. D.; Morais, C. M.; Rocha, J. *J. Am. Chem. Soc.* **2003**, *125*, 14573-14579.
- [5] Ananias, D.; Ferreira, A.; Carlos, L. D.; Rocha, J. *Adv. Mater.* **2003**, *15*, 980-+.
- [6] Ananias, D.; Rainho, J. P.; Ferreira, A.; Lopes, M.; Morais, C. M.; Rocha, J.; Carlos, L. D. *Chem. Mat.* **2002**, *14*, 1767-1772.
- [7] Ananias, D.; Ferreira, A.; Rocha, J.; Ferreira, P.; Rainho, J. P.; Morais, C.; Carlos, L. D. *J. Am. Chem. Soc.* **2001**, *123*, 5735-5742.
- [8] Rocha, J.; Ferreira, P.; Carlos, L. D.; Ferreira, A. *Angew. Chem. Int. Edit.* **2000**, *39*, 3276.
- [9] Kostova, M. H.; Ananias, D.; Paz, F. A. A.; Ferreira, A.; Rocha, J.; Carlos, L. D. *J. Phys. Chem. B* **2007**, *111*, 3576-3582.
- [10] Ananias, D.; Paz, F. A. A.; Carlos, L. D.; Geraldés, C.; Rocha, J. *Angew. Chem. Int. Edit.* **2006**, *45*, 7938-7942.
- [11] Rocha, J.; Carlos, L. D.; Paz, F. A. A.; Ananias, D.; Klinowski, J. In *Recent Advances in the Science and Technology of Zeolites and Related Materials, Pts a - C*; Elsevier Science Bv: Amsterdam, 2004; *154*; pp. 3028-3035.
- [12] Cunha-Silva, L.; Mafra, L.; Ananias, D.; Carlos, L. D.; Rocha, J.; Paz, F. A. A. *Chem. Mater.* **2007**, *19*, 3527-3538.
- [13] Shi, F.-N.; Cunha-Silva, L.; Sá Ferreira, R. A.; Mafra, L.; Trindade, T.; Carlos, L. D.; Paz, F. A. A.; Rocha, J. *J. Amer. Chem. Soc.* **2007**, *In Press*.