



	Experiment title: New Microporous Transition-Metal Heteropolyhedra Catalysts	Experiment number: CH-2155
Beamline: ID31	Date of experiment: from: 09 – March – 2006 to: 10 – March – 2006	Date of report: 26 – Feb – 2007
Shifts: 3	Local contact(s): Dr. Irene Margiolaki (E-mail: irene.margiolaki@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] *</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 15 years, our research group has been particularly active in the field of new microporous zeolite-type transition metal silicates and, more recently, in materials containing lanthanide centres. Since these compounds are usually isolated as microcrystalline powders, their structural details have eluded us for some time. This is because the powder patterns collected at the laboratory scale do not have enough resolution and, in many cases, are severely affected by preferential orientation, which significantly decreases the possibility to solve the structure of these compounds using powder data. The aim of this proposal was to collect high-resolution powder X-ray diffraction data for a number of materials we have been reporting over the years. It was expected that the high brilliance of the synchrotron source in combination with the increased line resolution would allow us to, finally, unveil the structure of many of these materials.

The collected powder X-ray diffraction patterns of the catalysts containing transition metal centres which were enumerated in the initial proposal (titanosilicate AM-18, $\text{Na}_6\text{Ti}_4\text{Si}_{12}\text{O}_{35}\cdot 11\text{H}_2\text{O}$; niobosilicate AM-11, $(\text{H},\text{Na})\text{Si}_5\text{NbO}_{13}\cdot 4\text{H}_2\text{O}$; chromosilicate AV-15, $\text{Na}_3\text{CrSi}_6\text{O}_{15}\cdot 4\text{H}_2\text{O}$; vanadosilicates AM-13, $\text{HNaCa}_2\text{Si}_{20}\text{V}_2\text{O}_{47}\cdot 11\text{H}_2\text{O}$, AM-14, $\text{Na}_2\text{Si}_4\text{VO}_{11}\cdot 3\text{H}_2\text{O}$, AM-15, $\text{Na}_6\text{Si}_{14}\text{V}_4\text{O}_{39}\cdot 9\text{H}_2\text{O}$, and AM-17, $\text{Na}_4\text{CaSi}_{10}\text{V}_2\text{O}_{27}\cdot 5\text{H}_2\text{O}$) revealed the presence of samples with relatively low crystallinity (low signal-to-noise ratio). The increased resolution of the pattern, when compared with those typically obtained at the laboratory scale, also revealed the presence of innumerable impurities and/or polymorphic phases. For many of these samples we are still trying to obtain reliable unit cell indexations which could allow us to, on the one hand, proceed with a full Rietveld refinement of the desired phase and, on the other, identify the impurities present. During acquisition of data for some vanadosilicate samples it was also found that the synchrotron beam was modifying structurally the samples, most probably due to redox reactions associated with the vanadium

metallic centres. From the collected data for this series of samples, we are now trying to rationalize the synthesis in order to produce samples with lower content of impurities.

During the allocated experimental time powder data for a new material, which was formulated *a posteriori* as $\text{Eu}_2(\text{SiO}_4\text{H})(\text{OH})_2(\text{H}_2\text{O})\text{Cl}$, was also collected (the wavelength was fixed at $0.80172(3) \text{ \AA}$) which ultimately allowed us to solve and refine the structure (see Figure 1). The powder pattern was indexed using DICVOL04 [$a = 8.28651(4) \text{ \AA}$, $b = 12.66540(6) \text{ \AA}$, $c = 7.09450(3) \text{ \AA}$, $V = 744.6(1) \text{ \AA}^3$, space group $Pbcm$] with high figures-of-merit [$M(25) = 233.2$ and $F(25) = 976.6$; zero shift of 0.0027°]. This new layered material was isolated as nanoparticles and fully characterised for its physico-chemical properties. In particular, this material displays efficient and tuneable photoluminescence properties (such as energy transfer between Gd^{3+} and Eu^{3+} centres). All this information and properties were systematised in the form a manuscript recently submitted to an international journal with a high-impact factor.

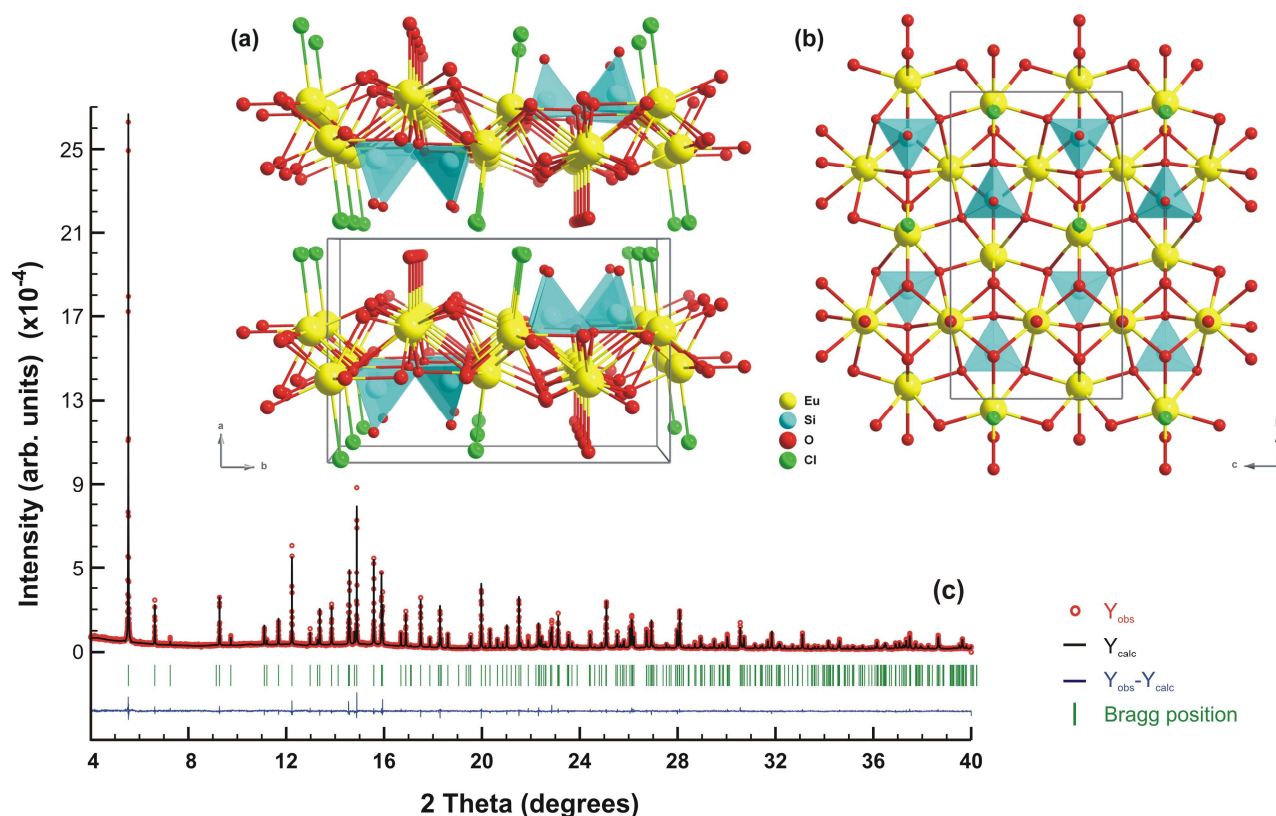


Figure 1. Perspective views along the (a) [001] direction of the crystal packing of $\text{Eu}_2(\text{SiO}_4\text{H})(\text{OH})_2(\text{H}_2\text{O})\text{Cl}$ and (b) towards the bc plane showing a top view of the $[\text{Eu}_2(\text{SiO}_4\text{H})(\text{OH})_2(\text{H}_2\text{O})\text{Cl}]_\infty$ layer. (c) Final Rietveld plot (from powder synchrotron XRD data).

Data were also collected for a novel strontium silicate compound (isolated from hydrothermal synthesis – Sr1) and the product obtained from its calcination at 700°C (Sr1_700). Both patterns could be indexed using DICVOL04 and the structures have been solved and refined using Fullprof.2k: for Sr1, $a = 22.715 \text{ \AA}$, $b = 5.898 \text{ \AA}$, $c = 3.784 \text{ \AA}$, space group $Immm$, $M(15) = 145.8$ and $F(15) = 299.3$; zero shift of 0.0033° ; for Sr1_700, $a = b = 4.117 \text{ \AA}$, $c = 10.144 \text{ \AA}$, space group $P6_3/mmc$, $M(20) = 185.9$ and $F(20) = 241.$; zero shift of 0.0055° . Sr1 is a lamellar structure with water molecules occupying the interlayer spaces; Sr1_700 is instead a rather dense material with statistical disorder associated with the crystallographically independent SiO_4 tetrahedron. However, as found for the catalysts with transition metal centres, the samples also contained significant amounts of crystalline impurities (not observed in patterns collected with a conventional instrument). We are now trying to optimise the synthetic condition to, at least, reduce the amount of impurities.