ESRF	**Experiment titles:** **Anion exchange studies in photoluminescent clay-inspired Frameworks**	**Experiment number**: CH-3994
Beamline: BM01b	**Date of experiment**: from: 30 – Sept. – 2013 to: 03 – Oct. – 2013	**Date of report**: 04 – Apr. – 2014
Shifts: 6	**Local contact(s)**: Dr. Wouter van Beek (E-mail: wouter@esrf.fr)	*Received at ESRF:*

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Summary

This report concerns the experiment at the ESRF with reference CH-3994 for which a total of 6 shifts were allocated. Overall the experiment was very successful, permitting the collection of high-quality powder X-ray diffraction data sets. In addition, the local support from the contact at the ESRF was extremely good, providing useful advice on the experimental apparatus and conditions for each individual data collection. We strongly believe that a great deal of the success of this experiment was due to the combined useful advice of Dr van Beek on how to collect data, and to the great versatility of the beam line and easy of use of the software.

Currently, two publications are being prepared using the data sets collected during this experiment.

Introduction:

In the last two decades our research group at the University of Aveiro has focused its research interest in the development of novel lanthanide-based materials.[1-10] The main objective is to design and prepare in the laboratory novel photoluminescent compounds, for which a detailed knowledge of the structural features is of crucial importance so to fully understand the observed properties.

The main purpose of this experiment at BM01b, for which only 6 shifts were allocated, was to collect high-resolution powder data for a complex novel system prepared in our laboratories: a new phase, prepared in large scale as nano-sized crystals, could be thermally processed into a photoluminescent target possessing a different crystal structure. The features of both the parent and final compounds remained elusive and only high-resolution data could permit the structural elucidation from powder data.

Experimental Apparatus

All investigated samples were packed in glass capillaries (Φ = 1.0 mm), and mounted into the goniometer of BM01b (Figure 1). Data collection was performed at a wavelength of 0.505(2) Å and at the low temperature of 110 K so to avoid any possible radiation damage to the samples (Figure 2).

Because the main purpose of this experiment was focused on the structural solution of new complex system for which the crystalline structure was modified upon thermal treatment, long data collections were selected with special emphasis in the acquisition of high signal-to-noise ratio at high angles. In this way, only a handful of data sets could be collected in the 6 shifts used.

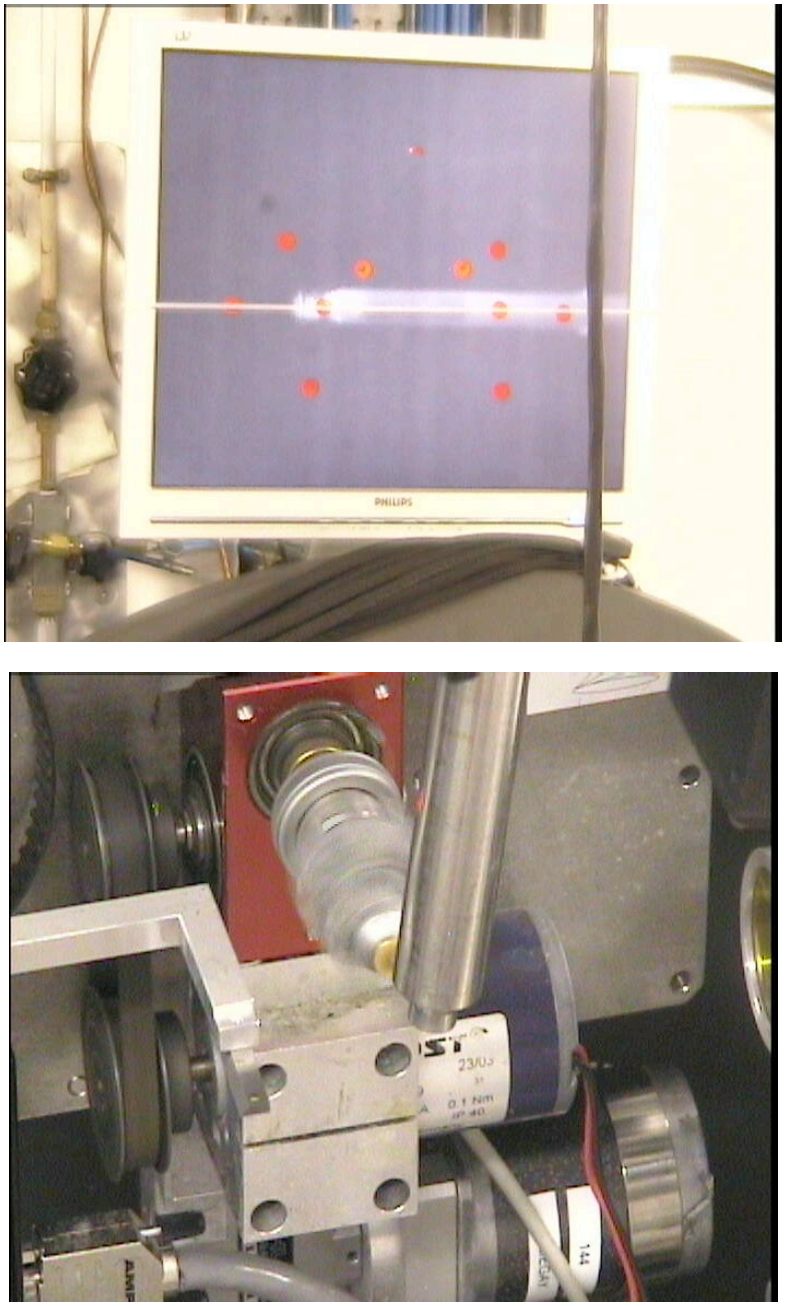

Figure 1. Picture of a spinning capillary in the beam.

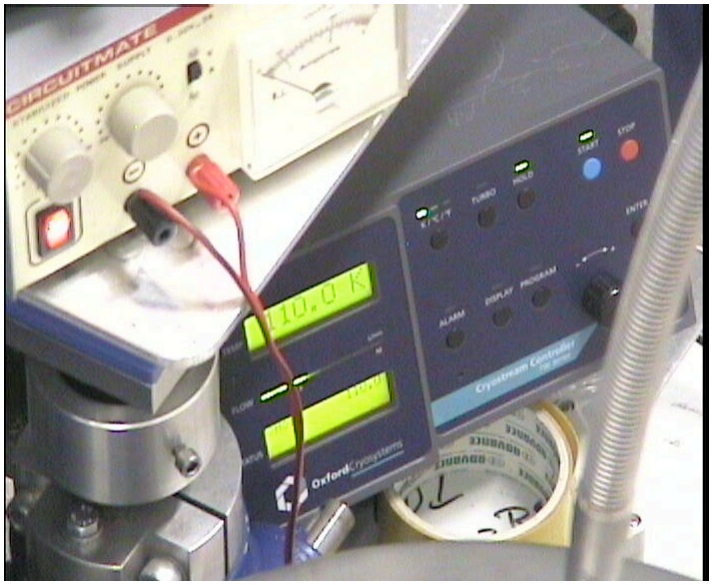

Figure 2. Picture of the cryostat controller showing a stable 110 K temperature for the data collection.

Results and Discussion

$KNa[Yb_2Si_3O_9]$

A high-resolution powder data set was collected for the final and functional material, coined hereafter as "target". The crystal structure of the target was indexed in the triclinic crystal system (unit cell volume of *ca.* 410 $Å^3$) with a final composition of $KNa[Yb_2Si_3O_9]$ (Figure 3). The Rietveld plot depicted in Figure 4 clearly shows a very good agreement between the experimental data set and the calculated pattern, ensuring a valid structure determination.

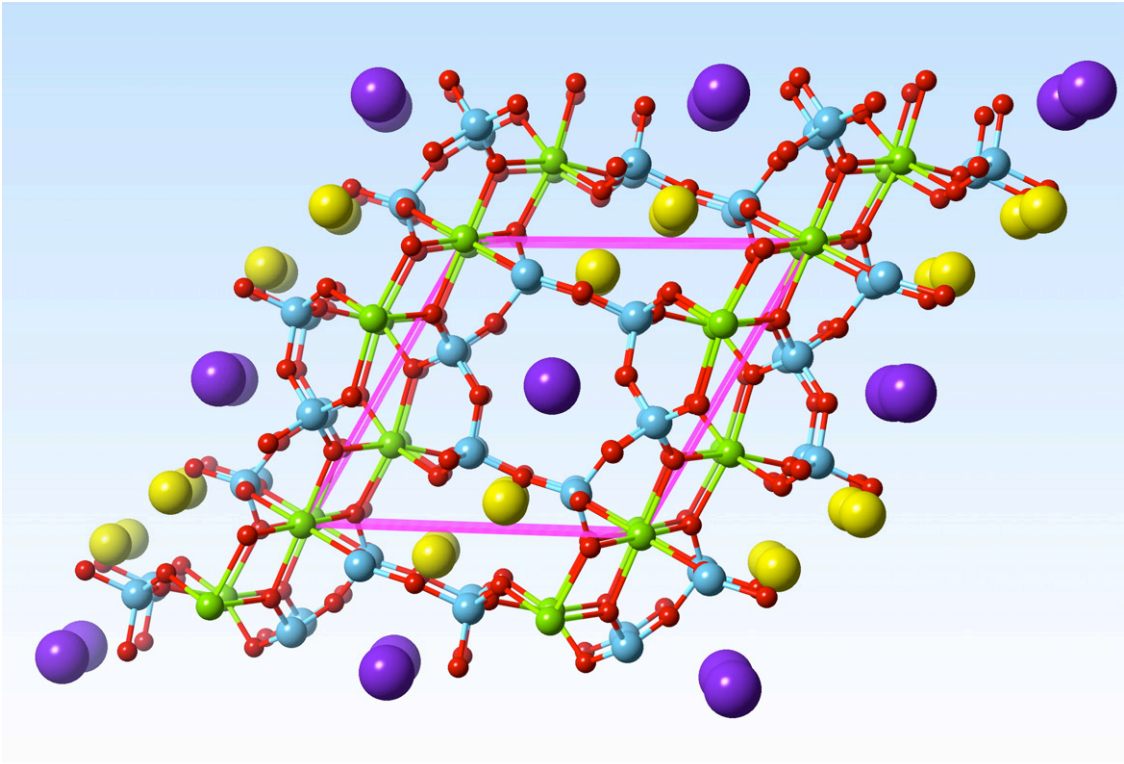

Figure 3. Schematic representation of the crystal packing of $KNa[Yb_2Si_3O_9]$.

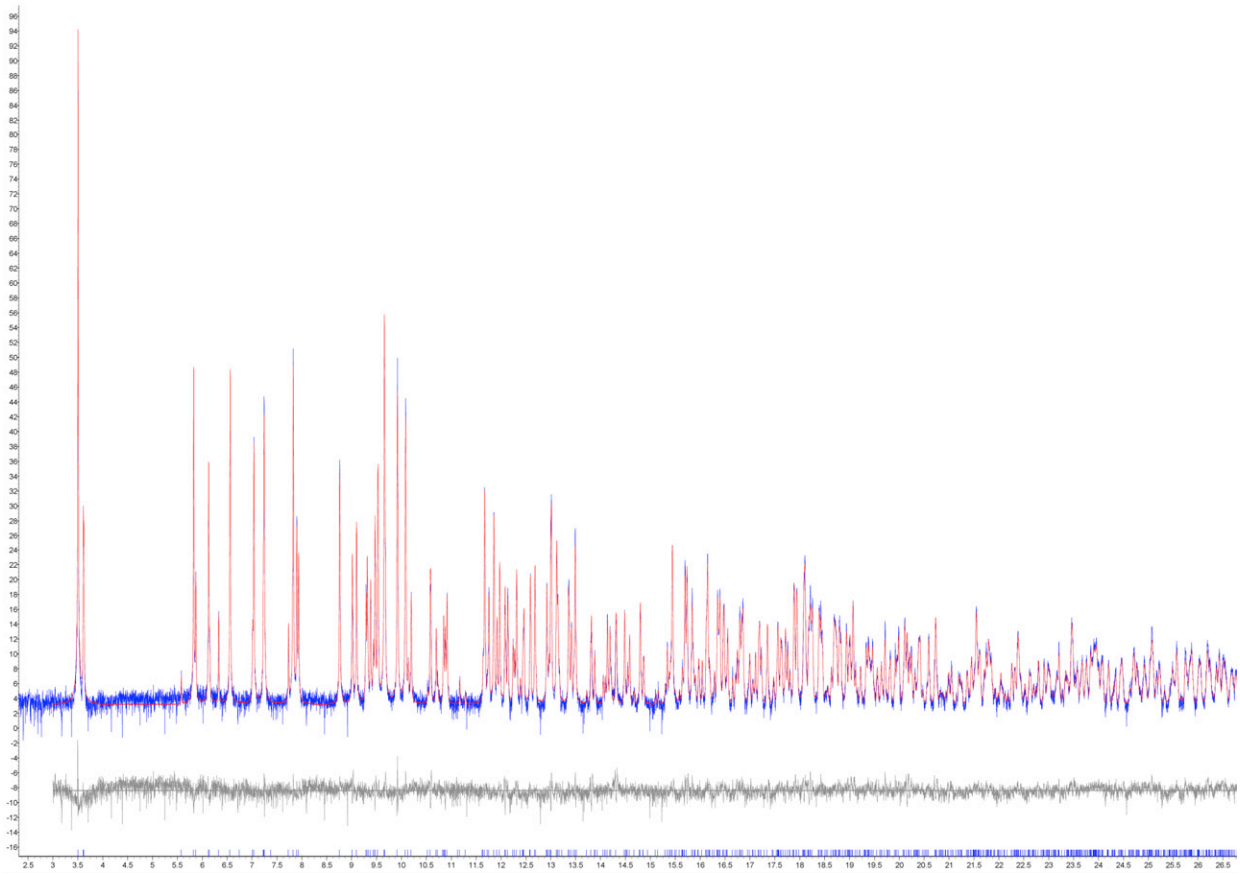

Figure 4. Final Rietveld plot of $KNa[Yb_2Si_3O_9]$.

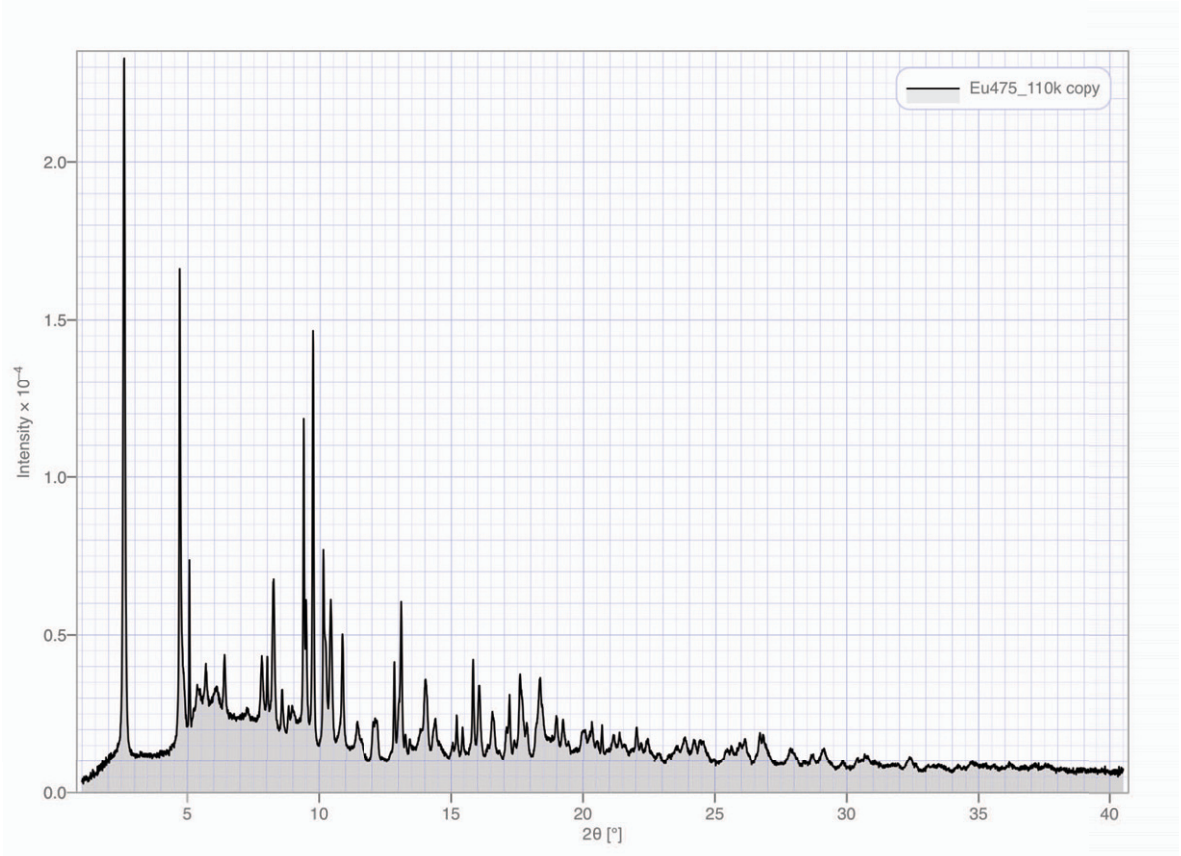

Figure 5. Powder pattern (BM01b) of the parent material used to prepare the target $KNa[Yb_2Si_3O_9]$.

A high-resolution powder X-ray diffraction pattern of the starting material from which $KNa[Yb_2Si_3O_9]$ was prepared was also collected (Figure 5). Preliminary data from our in-house instruments did not allow a sensible unit cell indexation, with the same being observed using the collected powder pattern at BM01b. Nevertheless, the increased resolution obtained at this beam line allowed discovering that the material is, most likely, a combination of two distinct polytypes of synthetic analogues tobermorite 11 Å as described by Merlino. At this moment we are collaborating with this retired Professor of Mineralogy to fully elucidate the composition of this starting material. In short, only the collection of a powder pattern at BM01b permitted the discover of the possible composition of the material used to synthesize the target $KNa[Yb_2Si_3O_9]$.

Y_2O_3:Eu

At the end of the experiment a small slot of time permitted the data collection of a powder pattern of a Eu^{3+}-dopped phase of nano-sized particles of Y_2O_3 with the aim to determine the average crystallite size (Figure 6). This is being done at the moment and it will be an important part of a manuscript under preparation.

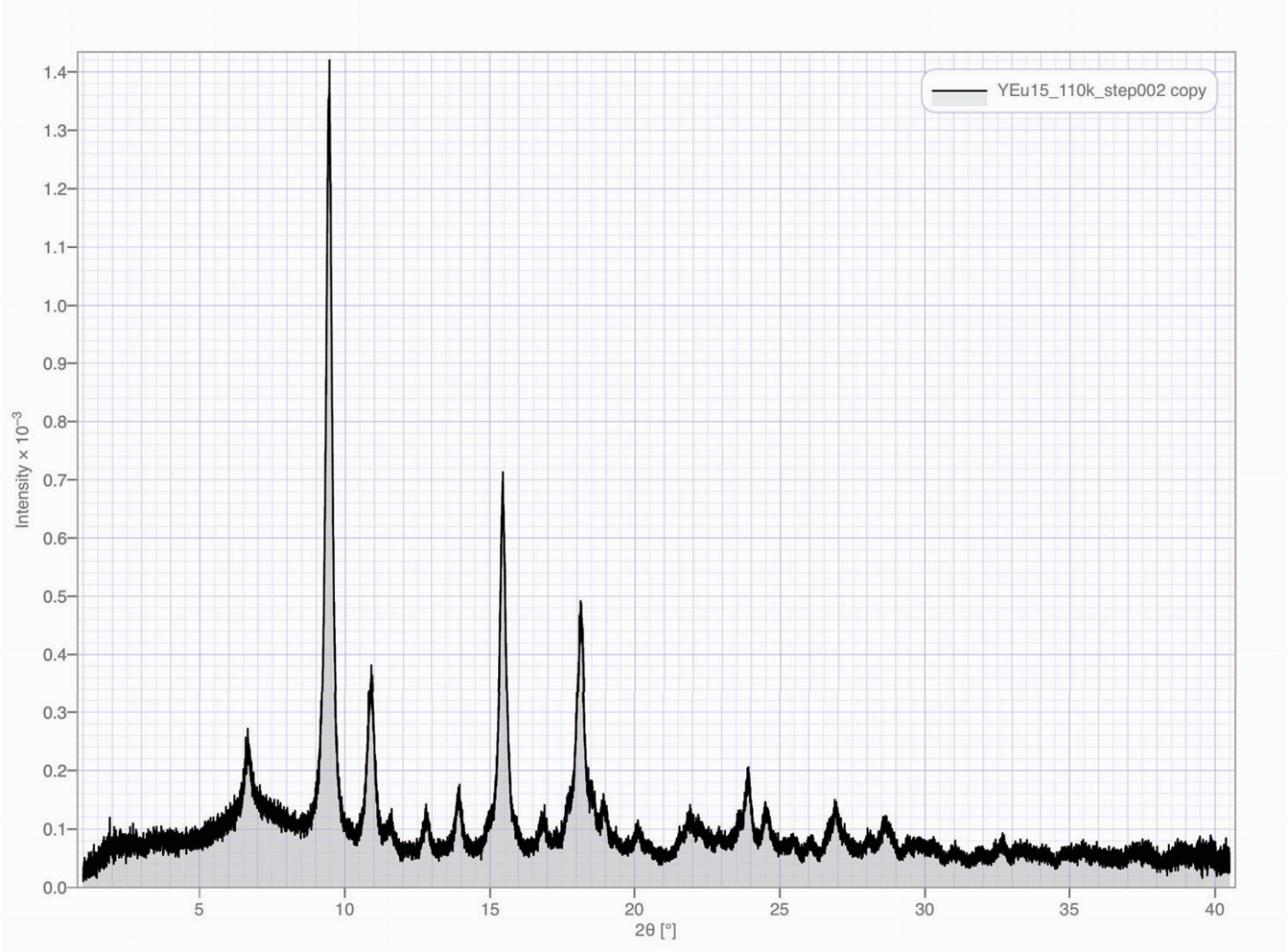

Figure 6. Powder pattern (BM01b) of nano-sized Y_2O_3 crystals dopped with Eu^{3+}.

Conclusions:

This short experiment at BM01b (6 shifts) permitted the collection of high-resolution data sets to fully elucidate the crystal structure of a novel, photoluminescent dense lanthanide silicate formulated as $KNa[Yb_2Si_3O_9]$. In addition, collected data also permitted us to identify the parent material of $KNa[Yb_2Si_3O_9]$ as a mixture of two distinct polytypes of tobermorite 11 Å. Data was also collected for nano-sized Y_2O_3 crystals dopped with Eu^{3+} for which we are investigating the average crystallite size.

In short, we believe that this was a very sucessful experiment from which two publications will arise in the foreseable future.

Acknowledgements

We are very grateful to our local contact (Dr. Wouter van Beek) for assistance with data collection and treatment, and also for very fruitful discussions. We also would like to thank Fundação para a Ciência e a Tecnologia (FCT, Portugal), FEDER, COMPETE and the Associated Laboratory CICECO.

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