Experimental report

14/02/2017

Proposal: **5-21-1102**

Council: 4/2016

Title: Fluorescent Centres in Scapolites

Research area: Materials

This proposal is a new proposal

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Samples: Scapolite

Instrument	Requested days	Allocated days	From	To
D2B	4	4	17/06/2016	21/06/2016

Abstract:

Our project involves modifying natural scapolites and synthesising similar materials in the laboratory to understand how we can control and use the fluorescent properties of the scapolites with an eventual aim to use these materials in cheap LED lighting. Scapolites are a common group of framework aluminosilicate minerals and materials with the general formula (Na,Ca,Li)4[(Al,Si)3Al3Si6O24](Cl,CO3,SO4,S2)
We need to investigate the detailed structure around the anions in relation to other factors such as Ca/Na/Li ratio, Al/Si framework ordering. We also intend to investigate how anion transformations/decompositions occur in these structures.

The scapolite series is a common group of framework aluminosilicate minerals and materials with the general formula $(Na,Ca,K)_4[(Al,Si)_3Al_3Si_6O_{24}](Cl,CO_3,SO_4)$, Fig 1. Scapolite forms solid solutions between the end-members marialite, $Na_4(Al_3Si_9O_{24})Cl$ = **Me0**, meionite, $Ca_4(Al_6Si_6O_{24})CO_3$ = **Me100**, and $Ca_4(Al_6Si_6O_{24})SO_4$ (= silvialite = **Me100**). Our recent interest in scapolites derives for their excellent fluorescent properties and the development of cheaper and environmentally benign alternatives to lanthanide based phosphors. To do this we needed to investigate the detailed structure around the sulfide anion how this structure stabilises and generates this species.

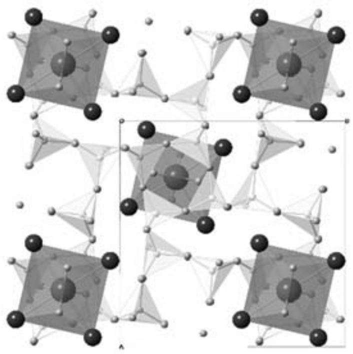


Fig. 1. The scapolite structure showing mixed anions (Cl/SO4) in coordination (dark grey square planes) to Ca/Na; framework shown as pale grey linked tetrahedra

The aim of this NPD experiment was to elucidate two main structural and reaction parameters of scapolites:-

(1) The role of cation environment around the anion and that of Al and Si ordering in affecting and controlling the fluorescence emission. It is noteworthy that fluorescent from the $[S_2]^-$ anion in sodalites is orange or red so the local square planar coordination (wholly or partly) by Ca^{2+}/Na^+ must control the emission spectrum and drive it to lower energies. This colour shift can also be controlled through ion exchange of Na^+ with Li^+. The cation arrangement is also likely to be associated with ordering of Al and Si in the framework as mentioned previously.

(2) Secondly the reaction chemistry of the anions inside the scapolite cage. While previous work indicates that carbonate doesn't decompose until 1100°C – some literature reports would indicate that disordering and decomposition of carbonate and sulfate occurs at much lower temperatures. The reductive decomposition of sulfate to $[S_2]^-$ provides a key route to fluorescent scapolites.

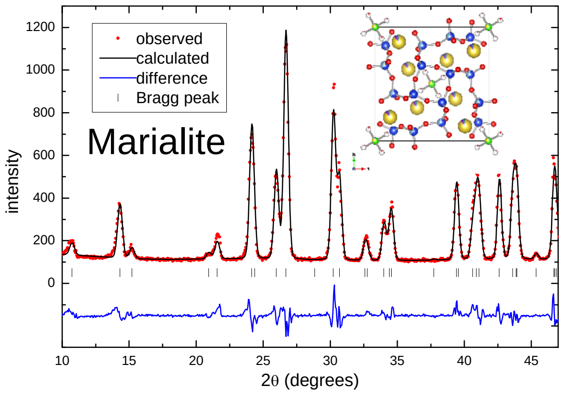
Five different mineral and material compositions were selected for study on D2B ($\lambda = 1.594$ Å) , namely

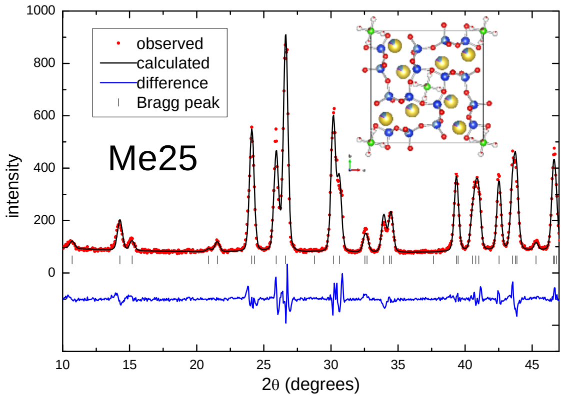
Meionite(NF), $Ca_4(Al_6Si_6O_{24})CO_3$ = **Me100**
Marialite (NF) $Na_4(Al_3Si_9O_{24})Cl$ = **Me0**
$(Na_{3.2}Ca_{0.8})[(Al,Si)_3Al_3Si_6O_{24}](Cl,CO_3)$- non fluorescent **= Me25**
Wernerite **(**Fluorescent**)** $(Na_2Ca_2)[(Al,Si)_3Al_3Si_6O_{24}](Cl,CO_3,SO_4, S_2)$ = **Me50**
Li exchanged Wernerite $(Li_2Ca_2)[(Al,Si)_3Al_3Si_6O_{24}](Cl,CO_3,SO_4, S_2)$ = **Li-Me50**

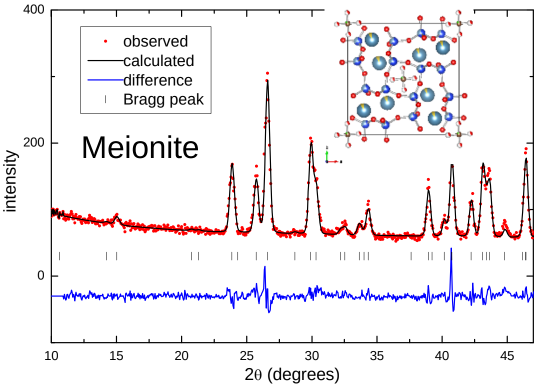
The data collections were divided in two parts, related to the key issues described above

(1) Powder diffraction data for all of the minerals and materials were obtained at room temperature (RT). The Rietveld refinements of the marialite, Me25 and meionite structures using their NPD data have been successfully completed some of these results are presented below. The best fluorescent material, the wernerite Me50 (and the derived Li-Me50 material) showed small levels of crystalline impurities and data analysis of this mixed phase material is still ongoing. Nevertheless, the impurity phases have been

identified and successful LeBail refinements have already been performed on both materials RT-NPD data.







(2) For the second part of the experiment, measurements were undertaken at variable temperatures between room temperature and 950°C to study any *in situ* decomposition behaviour of the scapolites. In total 40 NPD pattern were recorded on D2B. All of them have been analysed initially using the Le Bail extraction method and show that the scapolite *framework* is stable to at least 950 °C; no additional decomposition phase peaks were observed - regardless of the scapolite sample composition. Rietveld refinements have successfully been performed using the marialite variable temperature data, for which no decomposition of the anion was expected. For this phase the anion content and the atomic positions were, as expected, very similar across the temperature range and useful information on the thermal expansion of the different elements (framework and extra-framework) of the scapolite structure were extracted. For the other compound changes in peak intensities at high temperature indicate that more substantial changes in structure, probably associated with the carbonate or sulfate anion decomposition, may be occurring. Further analysis of these using mixed anion site models and Rietveld method profile refinement are in progress.

The experiment was completed as planned and high quality date obtained. Results obtained so far are very promising and we expect that this work will be at a publishable stage in few months.