



Experiment title: Structure solution of germanium-containing open framework materials	Experiment number: 25-01-1021	
Beamline: BM25A	Date of experiment: from: 02 March 2017 to: 04 March 2017	Date of report: December 2018
Shifts: 6	Local contact(s): Dr. Aida Serrano	<i>Received at ESRF:</i>

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Report:

Introduction

Zeolites constitute a technologically important class of microporous crystalline materials. Synthetic efforts targeting the discovery of new zeolite structures through the so call structure-direction effects need to be coupled to structural and computational studies aimed to shed light on the nature and mechanism of action of such effects. Important structure-direction effects that have received much attention in the last several decades include the use of organic structure-directing agents (OSDA), the use of germanium and the use of fluoride anions. This brief note reports on synchrotron diffraction experiments aimed at the detailed structural elucidation of open-framework silicogermanates and having multiple ultimate goals, including the determination of patterns of preferential location of Ge in different zeolites, with and without double 4 membered rings (D4R), the precise location of the organic structure-directing agents and that of the fluoride anions, as well as the structural elucidation of several new materials.

Experimental

Data were collected in capillary mode (0.8 or 1 mm internal diameter) using synchrotron radiation ($\lambda=0.56383 \text{ \AA}$) at room temperature. The 2θ range was varied according to the nature of the sample, but was generally 2-35°, (occasionally reaching 40°).

Results

One of our interests refers to the preferential location of Ge in the framework of the chiral zeolite STW, for which we have been able to synthesize the whole Si-Ge substitutional series (i.e. with $G_e = \text{Ge}/(\text{Ge} + \text{Si})$ from 0 to 1).¹ We had already reported the structure of the Si end-member,² and now determined those of three

materials with $Ge_f = 0.4, 0.6$ and 1.0 . Rietveld refinement proceeded smoothly, in the final stages without distance restrains. We also studied the whole series by a combined theoretical-experimental approach (including multinuclear MAS NMR, GULP simulations and DFT calculations). We found an overall good agreement between the experimental and theoretical trends in the preferential occupation of different crystallographic sites by Ge. However, the theoretical models showed sharper and more abrupt tendencies than found experimentally, which we interpreted as likely due both to limitations of the theoretical approach and to kinetic factors that allow metastable configurations to appear experimentally. The occupancies of sites determined by Rietveld refinement are listed in Table 1 and one of the Rietveld plots is shown in Figure 1.¹

Table 1. Refined occupancies of Ge in different sites of the STW framework with two different overall Ge contents. Sites T1 to T4 belong to double 4-membered rings.

Site	$Ge_f=0.4$	$Ge_f=0.6$
T1	0.552	0.748
T2	0.555	0.735
T3	0.388	0.584
T4	0.393	0.591
T5	0.092	0.215

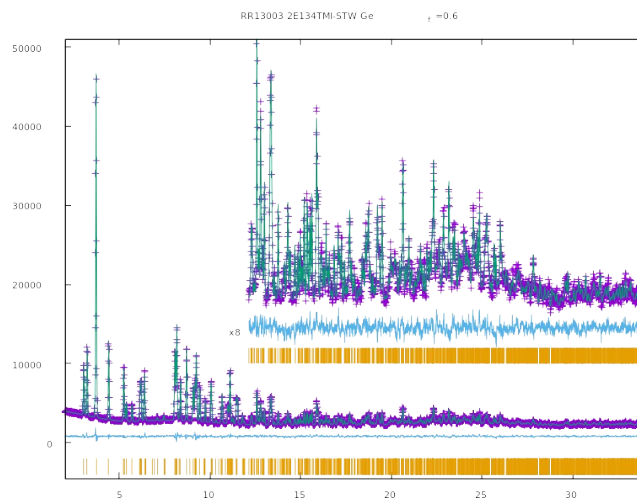


Figure 1. Rietveld plot for a STW zeolite with a $Ge_f=0.6$.

We also investigated the same STW zeolite synthesized by using a new OSDA consisting of two 1,2-dimethylimidazolium moieties linked by a linear chain of four methylene units. This type of OSDA is interesting because each imidazolium moiety sits in a single zeolite cavity, so the location of the OSDA span more than one cavity and, hence, introduction of chirality in the chain could impose the crystallization of a particular enantiomer of this chiral zeolite.³ Also in this case there was a significant enrichment in Ge in specific positions (D4R).⁴

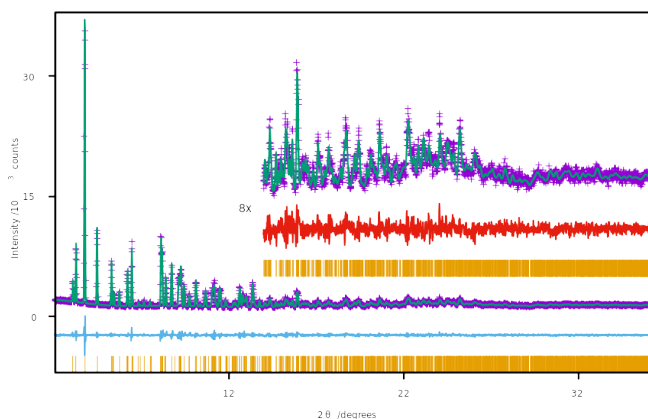
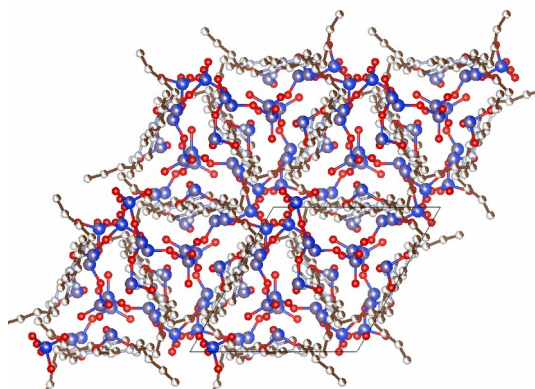


Figure 2. Structure (left) and Rietveld plot (right) of a STW zeolite synthesized using a dication consisting of 1,2-dimethylimidazolium moieties linked by a tetramethylene chain.

We also solved the structure of the new zeolite HPM-7,⁵ synthesized with a dication similar to the one above but made with a longer linker (either eight or ten methylene unit). HPM-7 is isostructural to the recently reported PKU-16,⁶ synthesized with a completely different OSDA. The structure presents an unusual 3D

system of large pores with 12MR pores along [001], and the infrequent 11MR pores along [110] and [1-10] (Figure 3).

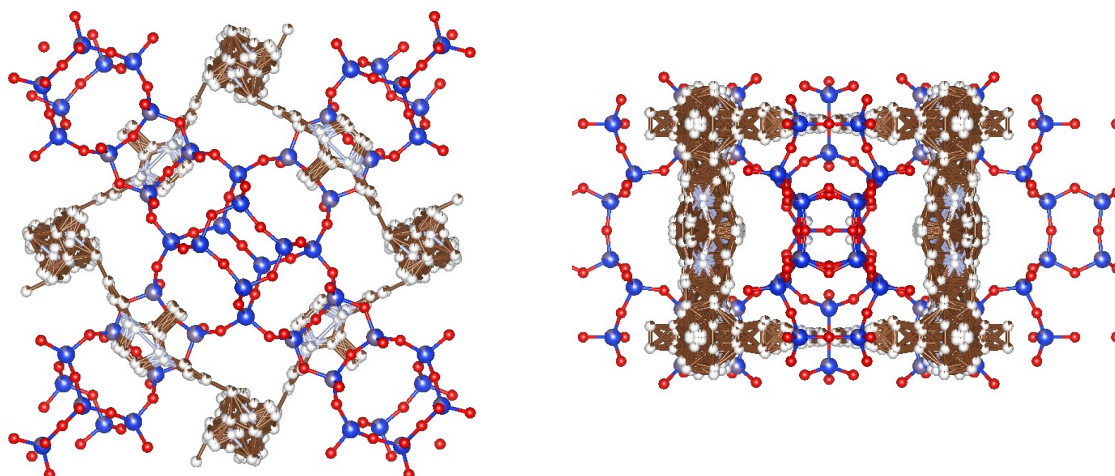


Figure 3.- The structure of HPM-7 along [001] (left) and [1-10] (right) showing the 12MR and 11MR pores, respectively. Several symmetrically equivalent dications are shown.

To complete the work related to this experiment we are now performing the structural analysis of zeolites HPM-6 and CIT-7.

References

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