ESRF	**Experiment title:** IXS Studies of the Single Crystal Elastic Constants of Zeolites	**Experiment number**: HS-3473
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Report:

The aim of this experiment was to measure the single crystal elastic constants of a zeolite that had been prepared as unusually large, millimetre-sized single crystals, using inelastic X-ray scattering (IXS). There is a distinct lack of experimental data in the literature concerning the elastic properties of zeolites and our results add to knowledge of the structural flexibility of this important family of materials. We have also demonstrated the applicability of this technique for measuring elastic constants of three-dimensional framework structures. The work forms part of an EPSRC funded project (£324k, 2005-2009) 'Inorganic Network Structures Exhibiting Unusual Negative Behaviours' supporting a post-doc and PhD student.

Zeolites are crystalline microporous solids whose three-dimensional frameworks are constructed from corner-sharing AlO_4 and SiO_4 tetrahedra. Electronic neutrality is provided by cations such as sodium, protons (to give the acid form of the zeolite) or organic cationic species, which may have been used in the synthesis procedure. Properties such as ion-exchange and adsorption are derived from a variety of channels and cages in the structures, through which small molecules or ions can move. Zeolites are used industrially as catalysts, where the internal space can be used to control the formation of a desired reaction product. As a result of their structural flexibility some zeolites exhibit negative thermal expansion,[1,2] and it is possible that interesting elastic behaviour may also be a characteristic feature.[3]

In spite of their industrial use and wide research interest there is little reported experimental work on the elastic properties of this class of materials. Knowledge of elastic behaviour of silicate materials is also of importance for the validation of computer simulations which have widely been used to predict and explain many properties of zeolites.[4,5] The lack of data is largely due to the difficulty associated with obtaining suitable specimens: conventional zeolite synthesis generally forms polycrystalline samples, whereas for elasticity measurements large single crystals are desired. We have successfully synthesised large crystals of the zeolite analcime (structure type **ANA**), $|Na^{+}_{16} (H_2O)_{16}| [Al_{16}Si_{32} O_{96}]$, illustrated in figure 1. This is a relatively simple zeolite framework with a cubic structure, and so is ideal to test the feasibility of using IXS as a tool for measuring the elastic constants of zeolites. We have previously obtained elastic constants *via* Brillouin light scattering,[6] which permits a comparison of the techniques to be made.

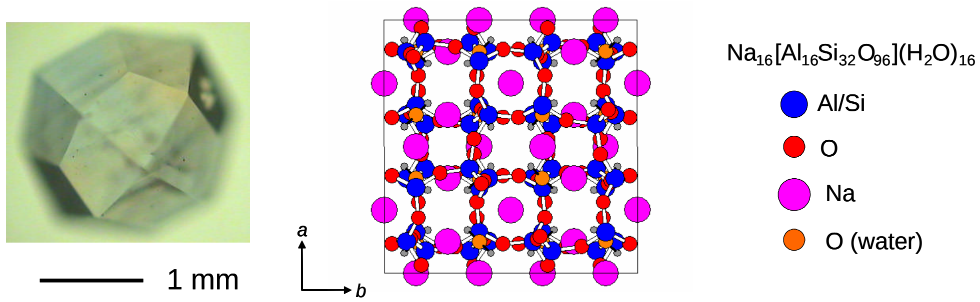

Figure 1: Single crystal specimen of the zeolite analcime, whose structure is shown on the right.

During the IXS experiment the instrument was operated at 17794 eV, providing an overall energy resolution of 3.0 meV full-width-half-maximum (FWHM). Direction and size of the momentum transfer were selected by an appropriate choice of the scattering angle and the sample orientation in the horizontal scattering plane. The momentum resolution was typically set to 0.28 nm^{-1} and 0.84 nm^{-1} in the horizontal and vertical plane. The dimensions of the focused x-ray beam were 250 x 60 μm^2 (horizontal x vertical, FWHM). The experiment was performed in transmission geometry. IXS scans were recorded in the proximity of the (800) and (044) Bragg's reflections in HHL reticular plane. Example scans are shown in figure 2.

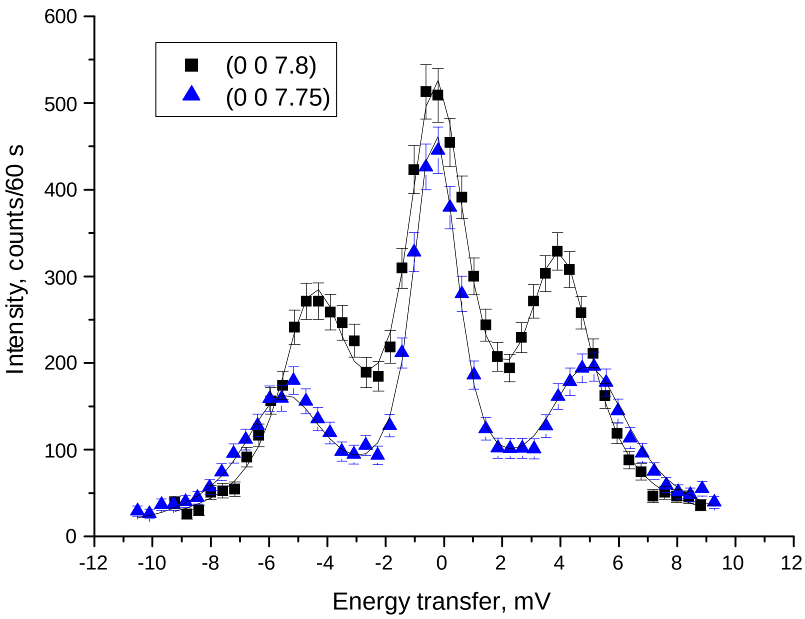

Figure 2: Example of data collected in the IXS experiment.

Sound velocities were obtained from plots of the excitation energy with reduced momentum transfer and from these the three elastic constants (C_{11}, C_{44} and C_{12}) were determined. These are given in table 1, along with values obtained from Brillouin scattering for comparison.

Table 1: Elastic constants (Cij) and values of Young's modulus (E), shear modulus (G) and Poisson's ratio (ν) for analcime.

	C_{11} (GPa)	C_{44} (GPa)	C_{12} (GPa)	E (GPa)	G (GPa)	ν
IXS (± 5%)	115.5	33.3	23.2	107.7	33.3	0.167
Brillouin scattering[6]	112.5 ± 1.1	27.9 ± 0.3	33.4 ± 0.4	97.2	27.9	0.229

The value for C_{11} is equal to that obtained in the Brillouin light scattering experiment within experimental error,[6] however there is some discrepancy between the values for C_{44} and C_{12}. IXS gives a higher value for C_{44} than Brillouin scattering, whereas C_{12} is lower. Currently we are unsure as to the origin of this discrepancy, however possible sources include localised heating in the Brillouin experiment, or some differences in the behaviour of the water molecules in the zeolite. Further data analysis is in progress.

In summary, we have demonstrated that IXS can be used to determine the elastic constants of zeolite single crystals. A paper describing this work is currently in preparation.[7] We hope to extend this technique to look at more structurally complex framework materials of lower symmetry as part of ongoing investigations into the way such materials behave under the application of directional forces.

References

1. M. P. Attfield and A. W. Sleight, Chem. Commun., 601 (1998).
2. P. Lightfoot, D. A. Woodcock, M. J. Maple, L. A. Villaescusa and P. A. Wright, J. Mater. Chem. **11**, 212 (2001).
3. J. N. Grima, R. Jackson, A. Alderson and K. E. Evans, Adv. Mater. **12**, 1912 (2000).
4. J. D. Gale, J. Chem. Soc., Faraday Trans. **93**, 629 (1997).
5. C. R. A. Catlow, Curr. Op. Solid State Mater. Sci. **7**, 1 (2003).
6. C. Sanchez-Valle, S. V. Sinogeikin, Z. A. D. Lethbridge, R. I. Walton, C. W. Smith, K. E. Evans and J. D Bass, J. Appl. Phys. **98**, 053508 (2005).
7. *Single crystal elastic constants of the zeolite analcime measured by inelastic X-ray scattering*, Z. A. D. Lethbridge, R. I. Walton, A. Bossak and M. Krisch, in preparation.