



	Experiment title: ZEOLITES UNDER PRESSURE: POTENTIAL NEW MATERIALS FOR CATALYSIS AND NANOENGINEERING	Experiment number: HS 2290
Beamline: BM01 A	Date of experiment: from: 04 February 2004 to: 08 February 2004	Date of report: February 24, 2005
Shifts: 12	Local contact(s): Prof. Vladimir DMITRIEV	<i>Received at ESRF:</i>

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Report:

Thanks to their peculiar structural and crystallochemical features, zeolites are extremely important in many fields of catalysis, synthesis, refining processes, environmental applications and so on. This versatile nature comes from the presence of voids – channels and / or cavities - within the (Si, Al) structure, and the possibility to host various compounds inside such cavities. Such features provide the zeolites with interesting properties of ion exchange, reversible dehydration and rehydration ability, molecular sieving performance against mixtures of isomeric compounds, and so on.

The extensive use of these materials in the most different sorts of chemical processes has required exhaustive studies about their response to non standard conditions, especially heating and dehydration (Alberti, 2004). On the other hand, their response to high pressure is still under investigation, and the literature in this sense is still limited. Yet, this aspect is particularly critical, as the response of a zeolite species to compression, in terms of how the cavities are (or are not) deformed and how the extraframework cations and water molecules are rearranged, could deeply change the physical properties of the zeolite itself, and therefore make the compressed material suitable for a new use and application (Secco and Huang, 1999)

Experimental

The behaviour of Gismondine, LiABW and dehydrated bikitaite was explored by means of X ray diffraction at beamline BM1A (SNBL). The compression was achieved by using a Diamond Anvil Cell, with pressure calibration through the ruby fluorescence (Mao et al., 1986). Different transmitting media were used: Silicon oil and propane-isopropane as non-penetrating pressure transmitting media, while water and methanol used as penetrating ones; LiABW was tested with all of them, in a view to compare the results on the same species but with different P transmitting media.

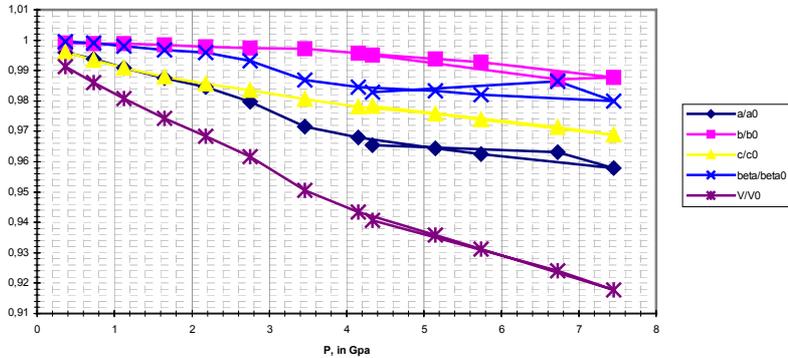
The pressure range applied spans from room pressure to about 10 Gpa. The data collections were performed with an incident wavelength of 0,7 Å, by means of a MAR 345 (pixel size 100 mm), and the two-dimensional images were turned into 2θ-scan with the FIT2D software (Hammersley et al., 1996). The 2θ accessed range is 0 – 36°.

Results

The data obtained from processing and refining provided the trends reported in the figures below.

Gismondina shows a regular trend, all of the cell parameters regularly decrease; by measuring some reverse pressure step, we also observe a rather regular and reversible behaviour. $K_0 = 63,8(0,2)$ GPa, $K_p = 5,2(0,3)$ (Birch 1952). The structural interpretation of the cell parameters variations will be derived by combining the experimental data with Molecular Dynamics Simulations.

Figure 1: Gismondine in Silicon Oil: normalized cell parameters
Space Group: $P2_1/c$



The data from the anhydrous bikitaite sample show an even more interesting result: bikitaite undergoes a phase transition at about 3GPa, with redoubling of the parameter a . EoS parameters before the phase transition for anhydrous bikitaite in Silicon Oil are: $K_0 = 21,5(0,1)$ GPa, $K_p = 21,0(0,8)$ (Birch 1952).

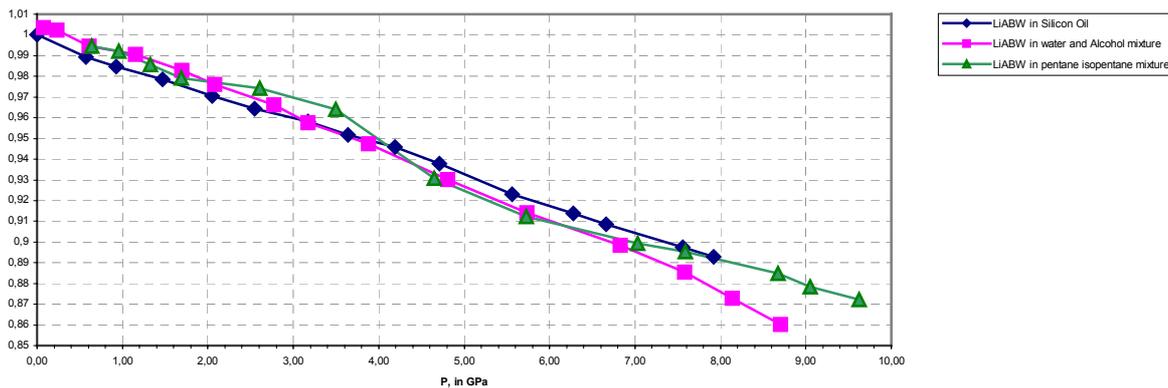
Three data sets were collected on LiABW using different P transmitting media. The trends obtained are quite regular for all the media, showing quite a regular decrease in volume with pressure.

LiABW in Silicon Oil (up to about 7 GPa): $K_0 = 68(2)$ GPa, $K_p = 0,6 (0,8)$;

LiABW in alcohol/water (up to about 7 GPa): $K_0 = 64,8 (0,8)$ GPa, $K_p = -0,69(0,11)$;

LiABW in pentane-isopentane (up to about 9 GPa) : $K_0 = 60 (5)$ GPa, $K_p = 1,5 (0,9)$;

Figure 3: LiABW, trend of V/Vo against p, in 3 different p transmitting media



References

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