EUROPEAN SYNCHROTRON RADIATION FACILITY

ESRF User Office

BP 220, F-38043 GRENOBLE CEDEX, France

Delivery address: 6 rue Jules Horowitz, 38043 GRENOBLE, France

Tel: +33 (0)4 7688 2552; fax: +33 (0)4 7688 2020; email: useroff@esrf.fr; web: http://www.esrf.fr

Application for beam time at ESRF – Experimental Method

This document should consist of a maximum of two A4 pages with a minimal font size of 12 pt.

Aims of the experiment and scientific background

α-Quartz is the most commonly used piezoelectric material. Its performance is limited at high temperature. Piezoelectric properties are limited in principle by the α–β phase transition at 846 K.

Structure-property relationships have been developed for α-quartz homeotypes in order to identify new materials with better intrinsic properties [1]. The most promising materials identified are $GaPO_4$ [2, 3] and $GaAsO_4$ [4, 5], which exhibit a high degree of structural distortion. Such an approach can in principle enable materials with tunable piezoelectric properties to be obtained by varying the chemical composition. We have demonstrated that single crystals can be grown over the entire compositional range in the $AlPO_4$-$GaPO_4$ system [6, 7].

In the same way we intend to study the SiO_2-GeO_2 system in order to increase the piezoelectric properties and the thermal stability of α-quartz material by the introduction of germanium in the structure. This project concerns a PhD student who has to grow $Ge_xSi_{(1-x)}O_2$ single crystals by hydrothermal method, the only method available to grow single crystals. For pure SiO_2, single crystals are grown in NaOH 1M solvent under 1500 bars at 350°C. The hydrothermal crystal growth process is based on the knowledge of the solubility and the complex ionic species which are at the origin of the crystallisation phenomenon. In the case of SiO_2-GeO_2 system, the solubility and the speciation will be modified by the presence of germanium.

XAS spectroscopy in fluorescence mode provides a very efficient way of in situ determination the solubility of the solid phase and the Ge local structure in its complexes and their interactions with the solvent. We will also follow the kinetics of the saturation which is an important parameter for the crystal growth restart.

The goal of this project is to quantify the atomic structure and stability of Ge species in supercritical dilute sodium hydroxide aqueous solutions. The role of the Ge/Si ratio at the critical-supercritical transition will also be investigated in these experiments.

Experimental method

The goal of the experiment is, as a function of temperature and pressure, to determine Ge(IV) concentration and Ge atomic environment in NaOH dilute solutions. Measurements will be conducted using a special high T-P cell (Institut Néel, Team of JL Hazemann, Grenoble) which operates both in transmission and fluorescence mode, and can be installed at FAME-BM30B beamline of ESRF. Details about the cell construction, operation and sample filling can be found elsewhere [8]**.** A carbon glass compartment serves as both solution container and windows for the beam passage (thickness ~ 0.1mm). The cell is inserted in a stainless steel autoclave with Be windows, pressurised with helium. Because pressure inside and outside of the cell is the same and imposed by an inert gas (He), any risk of solution leak or cell explosion at high temperature is excluded. This safety design can operate up to about 1000°C and 2 kbars, and allows XAS spectra acquisition for Ge-bearing solutions at concentrations as low as 0.1 millimol/L.

We have already prepared several compositions of the mixed system with the cristobalite structure or as a glass. Several parts of SiO_2-GeO_2 solid solution and appropriate amount of dilute NaOH solution will be placed in the cell, pressurised and heated. The filling of the cell will be made in order to reach about 1300 bars for a temperature range varying from 350 to 450°C. By comparison with Pokrovski's work [8], we will use a mineralizer (NaOH) which leads to an increase in the solubility. In consequence, the concentrations will be higher than 1millimol/L that makes the data acquisition easier: absorption edge height (proportional to the total Ge concentration and fluid density) in transmission mode, and ii) the after-edge spectrum (to extract structural information) provided a high photon flux (>10^{13} ph/sec) and sensitive detection in fluorescence mode. XANES and EXAFS spectra of the solutions will be recorded at the Ge K-edge (~ 11.1 keV) as a function of temperature to 500°C, at a pressure of about 1300 bars.

We intend to test three compositions in the solid solution (X_{Ge}= 0.1, 0.2 and 0.3) for two solvent concentrations (NaOH 0.5 and 0.2M/L). Time is necessary to start measurements (cell installation and beam adjustment need typically 1 to 2 shifts). Elsewhere, we need to reach the equilibrium for each temperature. A minimum of 5 temperature points will be measured with an equilibrium time of 2 hours for each. For each filling of the cell the global required time of experiment is 3 shifts. Thus, at least 18 shifts are required to perform runs under all the experimental conditions (6 fillings of the cell).

In order to obtain a good quality data and the necessary spectral resolution, the storage ring should operate in multibunch mode with a 200mA current. The beam line optics will incorporate a Si(220) double-crystal monochromator with sagittal focalisation (FAME-BM30B) allowing an energy resolution of about 1 eV at the Ge K-edge and a Rh-coated (FAME-BM30B) mirror for harmonic rejection. Fluorescence detection will require a Canberra 30-element detector (FAME-BM30B). The high X-ray flux and efficient beam focussing provided at FAME-BM30B beamline are particularly favourable.

Results expected

The proposed study will allow us to determine the solubility in situ which directly governs the crystal growth in the autoclave. It will be possible to understand how the solvent concentration plays a role on the Ge/Si ratio in the solution and in consequence on the composition on the crystal (under crystal growth conditions). In addition, it will be important for us to know the structure of the chemical species to best understand the chemical reactivity which takes place at the interface solid-liquid during the crystal growth at super-critical conditions. This step of the study is essential to control the crystal growth conditions in the aim to obtain single crystals of with the highest structural and chemical quality on which the piezoelectric properties of the material depend.

References

[1] O.Cambon, J.Haines, Structure-piezoelectric property relationships in α-quartz isoptypes: design and characterizations of high performance piezoelectric materials. *Proceeding of the 2003 IEEE International Frequency Control Symposium and PDA exhibition jointly with the 17th European Frequency and Time Forum (IEEE, Piscataway, NJ)*, pp. 650-653, 2003.

[2] P.Yot, O.Cambon, D.Balitsky, A.Goiffon, E.Philippot, B.Capelle, J.Detaint, Advances in crystal growth and characterizations of gallium orthophosphate, $GaPO_4$, *J. of Crystal Growth*, **224/3-4**, 294-302, 2001.

[3] J.Haines, O.Cambon, N.Prud'homme, G.Fraysse, D.A.Keen, L.C.Chapon, M.G.Tucker, High temperature, structural disorder, phase transitions, and piezoelectric properties of $GaPO_4$, *Phys. Rev. B*, **73**, 014103, 2006.

[4] O. Cambon, P. Yot, S. Rul, J. Haines, E. Philippot, Growth and dielectric characterization of large single crystals of $GaAsO_4$, a novel piezoelectric material, *Solid State Sciences*, 5, 469-472, 2003.

[5] O.Cambon, J.Haines, G.Fraysse, J.Detaint, B.Capelle, A.Van Der Lee, Piezoelectric characterization and thermal stability of a high-performance α-quartz material, gallium arsenate, *J.Applied Physics*, 97, 074110 1-7, 2005.

[6] J.Haines, O.Cambon, D.Cachau-Herreillat, G.Fraysse, F.E. Mallassagne Single crystal X-ray diffraction study of α-quartz-type $Al_{1-x}Ga_xPO_4$, *J. of Solid State Sciences*, **6**, 995-999, 2004.

[7] J.Haines, O.Cambon, G.Fraysse, A.Van der Lee, An x-ray powder diffraction study of the high temperature phase transitions in α-quartz-type $AlPO_4$-$GaPO_4$ solid solutions, *J. Phys. Condens. Matter*, **17**, 4463-4474, 2005.

[8] G.S. Pokrovski, J.Roux, J.L Hazemann, D.Testemale, An X-ray absorption spectroscopy study of argutite solubility and aqueous Ge(IV) speciation in hydrothermal fluids to 500°C and 400bars. *Chemical Geology*, 217, 127-145, 2005.