ESRF	**Experiment title: The effect of high-temperature on pressure-induced phase transitions and amorphization in the alpha-quartz-type solid solution $AlPO_4$-$GaPO_4$**	**Experiment number**: HD144
Beamline:	**Date of experiment**: from: 14/06/2007 to: 19/06/2007	**Date of report**: 18/02/2008
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Report:

Aims of the experiment and scientific background

The discovery of the pressure-induced amorphization of α-quartz at pressures above 15 GPa [1] generated a great deal of interest in the origin of this phenomenon, which has been the subject of numerous experimental and theoretical studies. Amorphous material has also been reported to be present in addition to high-pressure crystalline phases [2], which highlights the competition between transitions to crystalline and amorphous forms [3]. α-Quartz homeotypes (GeO_2, BeF_2, PON, ABO_4: A = B, Al, Ga, Fe; B = P, As) provide models for the high-pressure behaviour of silica and are also potential new materials with improved properties (i.e. piezoelectrics) [4]. Starting from the α-quartz- or α-berlinite-type structure (space group, $P3_121$, Z= 3) for AO_2 or ABO_4 compounds, respectively, transitions to amorphous and/or crystalline phases have been reported for various α-quartz-homeotypes [4, 5]. In the case of $FePO_4$ [6], for example, simultaneous transitions to a $CrVO_4$ structure and an amorphous form were observed at 2.5 GPa. This $CrVO_4$ structure with mixed 6:4 cation coordination is a stable high pressure form for various phosphates [4-7]; however, thermal activation is often necessary in order to obtain this form. Several solid solutions exist between α-quartz homeotypes. In the case of the $AlPO_4$-$GaPO_4$, an x-ray diffraction study indicated that there is complete static Al/Ga disorder, which may open the way to design materials with tuneable piezoelectric properties [8-10]. Up to the present, it is not known what influence pre-existent static disorder has on the competition between transitions to crystalline or amorphous high pressure phases. Our preliminary high pressure data obtained by laboratory x-ray diffraction indicate the formation of a new, unidentified, poorly crystallized phase [11]. The combined use of XAS and x-ray diffraction as a function of pressure and temperature in the present study has enabled us to better understand the competition between this new phase and other crystalline or amorphous forms.

Experimental method

We have studied a representative composition in the $AlPO_4$-$GaPO_4$ solid solution, $Al_{0.3}Ga_{0.7}PO_4$, and pure $GaPO_4$, as a function of pressure and temperature up to 32 GPa and 330°C by XAS and XRD on ID24 [High Press. Res. **23**, 301, (2003)]. High pressure and high pressure/high temperature XAS measurements were performed at the Ga K-edge

(10.447 keV). XRD patterns were obtained using a Mar Research imaging plate and analysed using the program FIT2D [12]. The sample was loaded in a diamond anvil cell equipped with 350 μm flat diamonds. The heating of the sample was performed using an external resistive heater. Sodium chloride and ruby were used as a pressure calibrants.

Results

Structural data both at short range (XANES+EXAFS) and long range (X-ray diffraction) were obtained as a function of P and T for $Al_{0.3}Ga_{0.7}PO_4$ and $GaPO_4$. $Al_{0.3}Ga_{0.7}PO_4$ was compressed at ambient temperature and then heated to 300°C at 25 GPa. The isotherm of $GaPO_4$ at 330°C was studied up to 32 GPa. The two materials behaved in a similar way. Taking $Al_{0.3}Ga_{0.7}PO_4$ as an example, a phase transition was observed from the α-quartz-type form at close to 10 GPa. A new crystalline phase was obtained, which was characterized by poor crystallinity and strong preferred orientation effects (Fig. 1a). This renders structural determination difficult. The XANES spectra (Fig. 1b) obtained provide evidence for an increase in the coordination number of gallium from 4 to 6. Analysis of the EXAFS data is in progress.

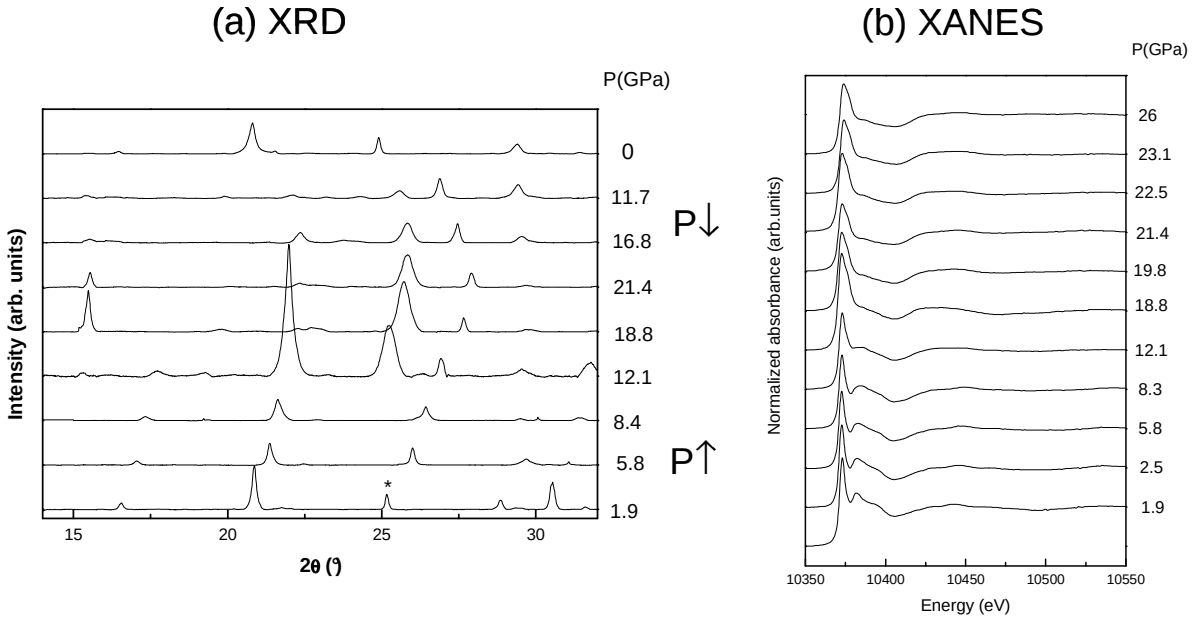

Fig. 1 X-ray diffraction (a) and XANES (b) data for $Al_{0.3}Ga_{0.7}PO_4$ as a function of pressure (*=NaCl).

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