

EUROPEAN SYNCHROTRON RADIATION FACILITY

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EXPERIMENT REPORT (Ref No: 25559)

XAS in-situ studies on hydrothermal growth of FeO₄-based crystals.

Introduction:

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 temperature stability of these homeotypes depends on the initial structural distortion. The most promising materials identified are GaPO₄ [2, 3] and GaAsO₄ [4, 5]. Yet the behavior in the α -phase is distinct for FePO₄ from those of other α -quartz homeotypes in that the angular variations are greater and do not scale with the initial structural distortion [6]. However, α - β phase transition for pure FePO₄ takes place at 980 K, which is not very high. It will be interesting to examine the solid solution of Fe and Ga phosphate to take advantage of highest transition temperature of Ga containing piezoelectric materials.

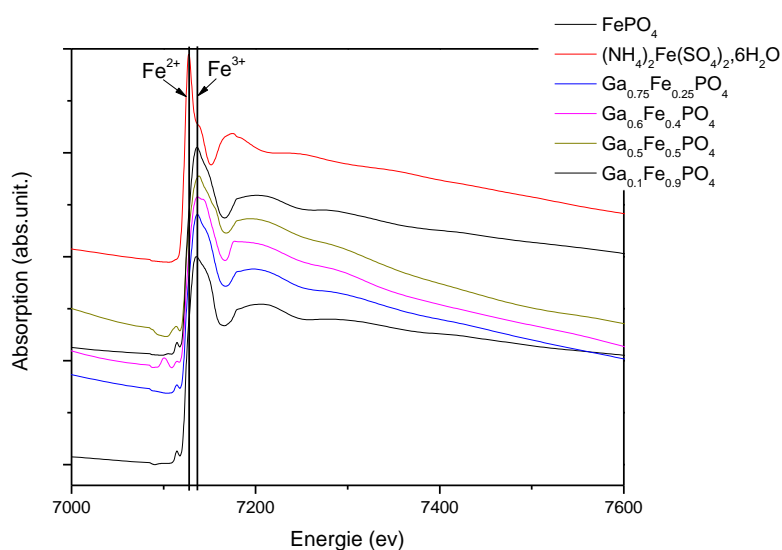
Due to these reasons, growth of α -quartz phase Ga_(1-x)Fe_xPO₄ single crystals is necessary to better understand the structure-property relationship and to design better materials for technological applications with high thermal stability and better quality factor. The stability conditions of Ga_(1-x)Fe_xPO₄ in α -quartz phase are present only during the hydrothermal growth. 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 Ga_(1-x)Fe_xPO₄ system, the solubility and the speciation will be modified by the presence of gallium.

Results obtained:

a) References:

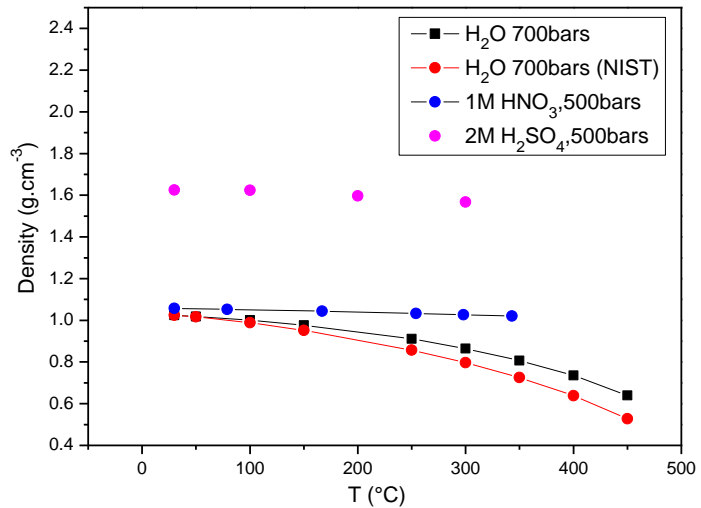
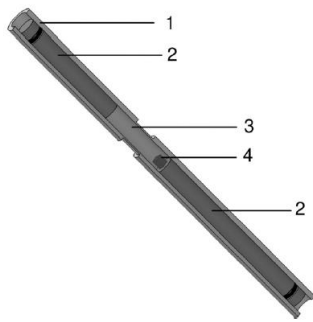
Compounds:

- FePO₄, α -quartz (4-fold coordinated Fe³⁺)
- Ga_xFe_{1-x}PO₄ α -quartz (4-fold coordinated Fe³⁺ with different Ga-contents)
- (NH₄)₂Fe(SO₄)₂·6H₂O : 6-fold coordinated Fe²⁺.



Transmission XAS spectra at room T and P.

b) Hydrothermal cell calibration:

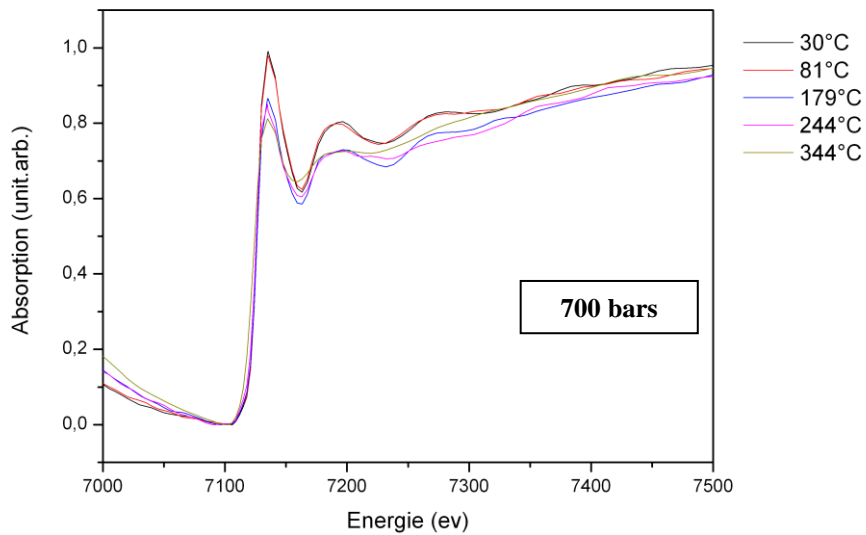


$$T = 0,8607 \cdot T_{\text{measured}} - 3,6837$$

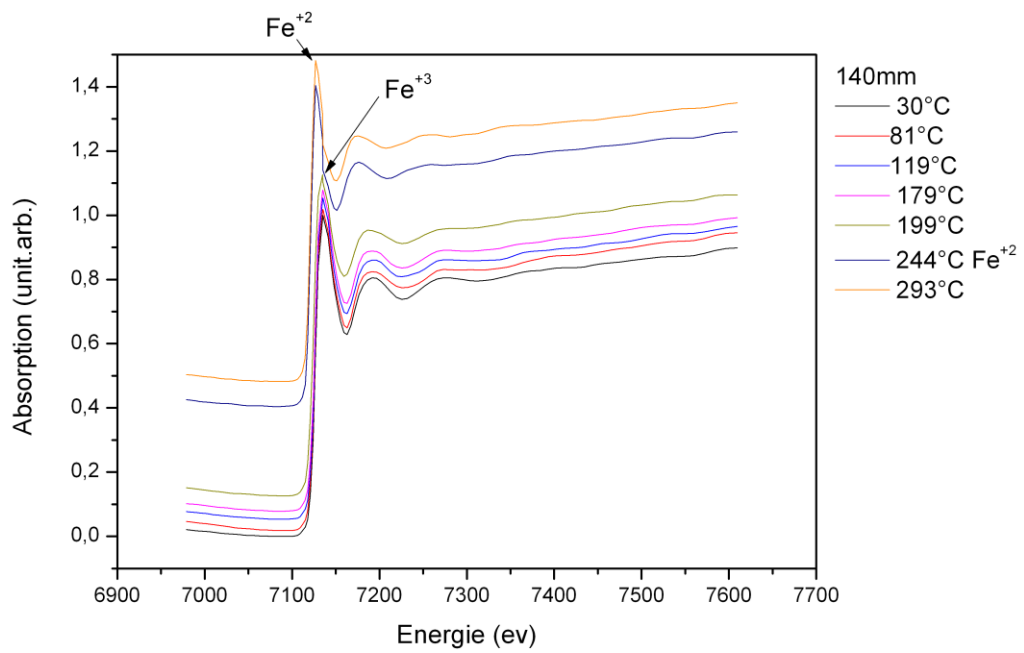
c) Calibration of experimental conditions.

Fe³⁺ solutions in KH₂PO₄/H₃PO₄ solvent:

Different solutions with different Fe³⁺ concentrations in buffer solution (KH₂PO₄/H₃PO₄ with pH=2) have been measured in fluorescence mode. In the aim to optimize the signal amplitude, different detector positions have been tested (D= 140, 180, 230 and 260mm from the autoclave)

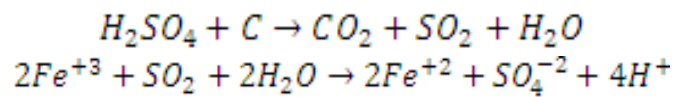


4M/L Fe³⁺ in pH=2 buffer solution as a function of temperature at 700bars



0.83M/L Fe³⁺ in H₂SO₄ 5M/L as a function of temperature at 500bars

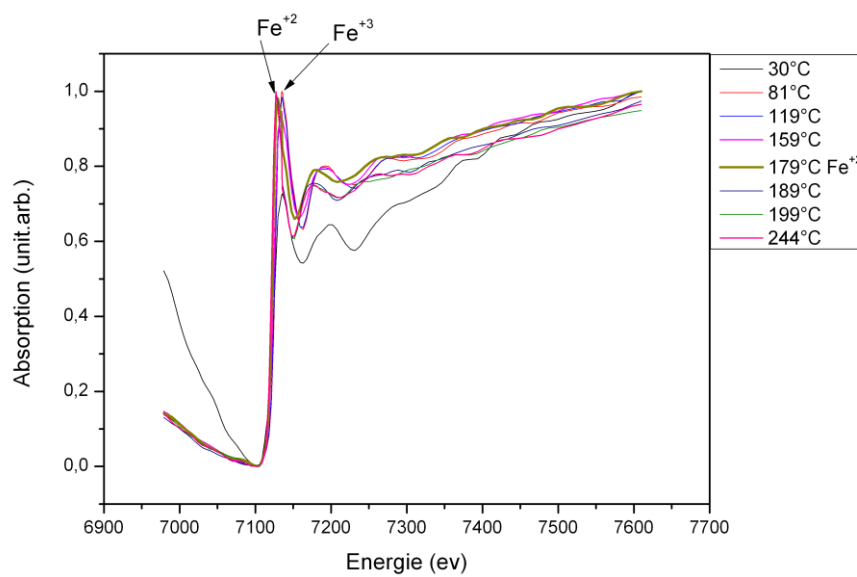
From 244°C, Fe³⁺ is reduced in Fe²⁺ by reacting with the carbon of the cell:



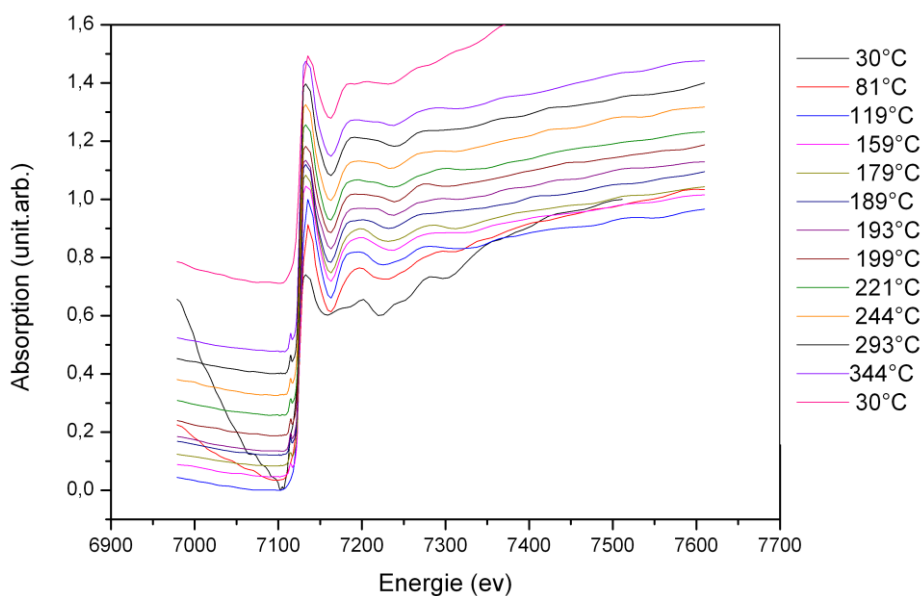
d) In-situ study of the dissolution of α-FePO₄:

Solid phase FePO₄ has been introduced in the cell with different solvents

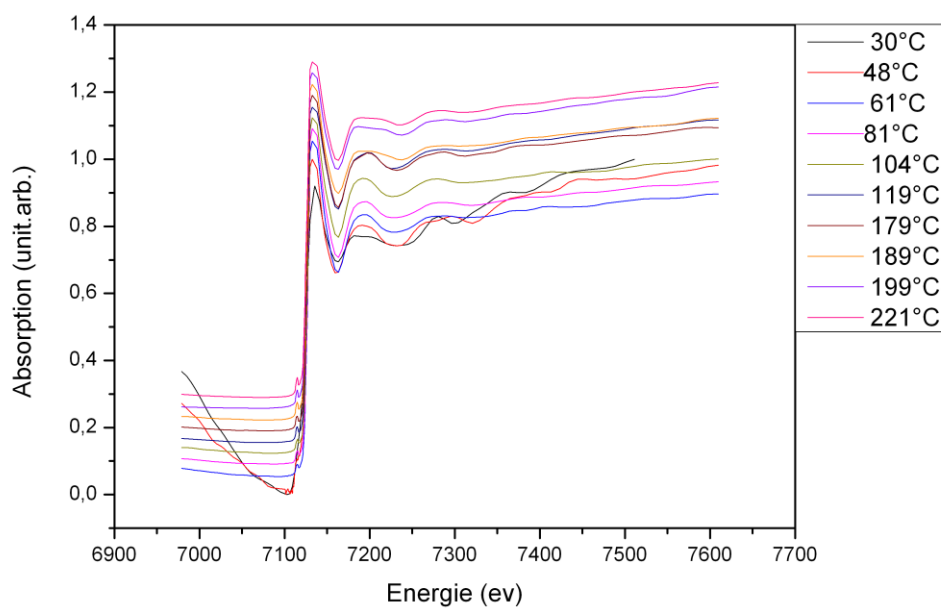
H₂SO₄ 2M/L at 500bars:



HNO₃ 1M/L at 500bars:

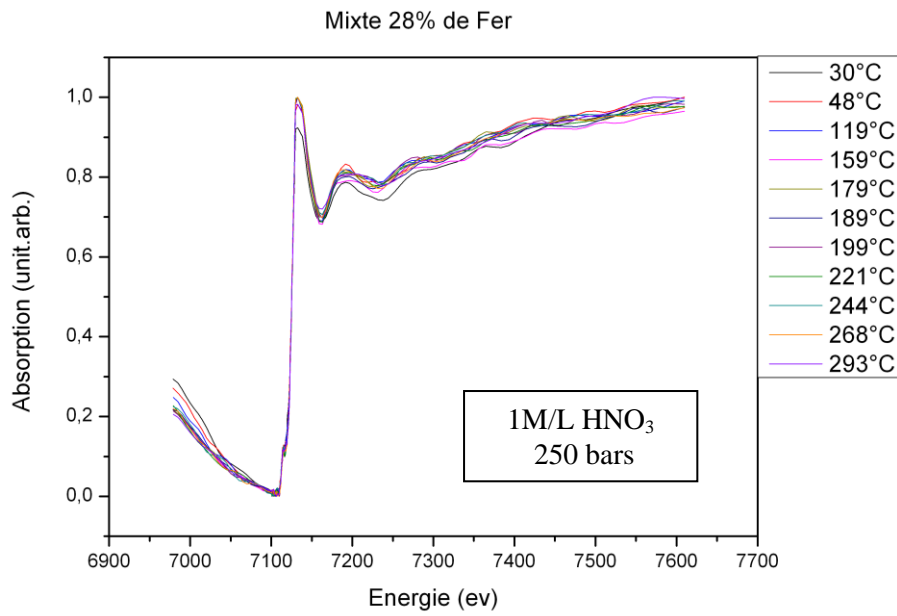


HNO₃ 1M/L at 250bars:



The use of nitric acid as the solvent allows stabilizing the oxidation degree +3 of iron in solution. Moreover, the study of the pre-edge could inform us about the coordination number around the iron in the same way than the EXAFS analyse.

e) **In-situ study of the dissolution of α -quartz $\text{Ga}_{0.72}\text{Fe}_{0.28}\text{PO}_4$:**



CONCLUSION:

During this experiment all data have been recorded at the Fe *K*-edge. The first results do not show the presence of the four-fold coordination around Fe during dissolution. Only one experiment of dissolution of the mixed solid solution $\text{Ga}_{(1-x)}\text{Fe}_x\text{PO}_4$ was performed for $x=0.28$. More experiments are necessary to study the effect of Ga^{3+} in solution which could govern the presence of FeO_4 tetrahedra in solution.