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Pressure effects on the solubility and crystal growth of α -quartz

F. LAFON and G. DEMAZEAU

*Laboratoire de Chimie du Solide du CNRS et Interface Hautes Pressions, LCS-CNRS-ENSCPB,
Université Bordeaux I, 33405 Talence cedex, France*

Abstract: Industrial α -quartz growth mainly refers to hydrothermal reactions with dissolution stage mass transport and crystallization at the interface between aqueous solution/seed. Experimental investigations on α -quartz dissolution with high pressure in different aqueous solutions (NaOH-1M, Na₂CO₃-1M) have underlined that : pressure parameter increases the solubility limit (s_l) of α -quartz for each investigated solution. In a high pressure range ($200 \leq P \leq 350$ MPa), Na₂CO₃(1M) seems a better solvent than NaOH(1M). Experimental studies on α -quartz growth rate versus pressure in both aqueous solutions NaOH(1M) and Na₂CO₃(1M) indicates the existence of a maximum for the kinetics of crystallization. In the case of Na₂CO₃(1M) a more complex variation of the growth rate is observed [1].

The use of pressure beyond 200 MPa could open new developments in α -quartz crystal-growth through :

- (i) a better knowledge of conventional solvents (NaOH and Na₂CO₃) in such a pressure domain,
- (ii) the investigation of new solvents more appropriate to reduce the concentration of chemical defects,

1/ INTRODUCTION

A considerable number of studies on the solubility of α -quartz crystals in water at elevated temperatures and pressures exist up to now [2,3]. However no determinations of α -quartz solubility limit in aqueous solutions such as NaOH(1M), Na₂CO₃(1M) using high pressures conditions from 200 MPa to 350 MPa at temperature of 400°C have been reported.

Because of the importance of pressure parameter on the crystal growth process during the hydrothermal preparation of α -quartz, the evaluation of pressure effect on the dissolution in different aqueous solutions was an important step.

As high frequency applications of α -quartz requires sheets with small thickness of the same order of size than the defects (such as inclusions, etch pits and dislocations, Fig. 1), so pressure parameter can promote new solvents for hydrothermal growth, especially for reducing their concentration.

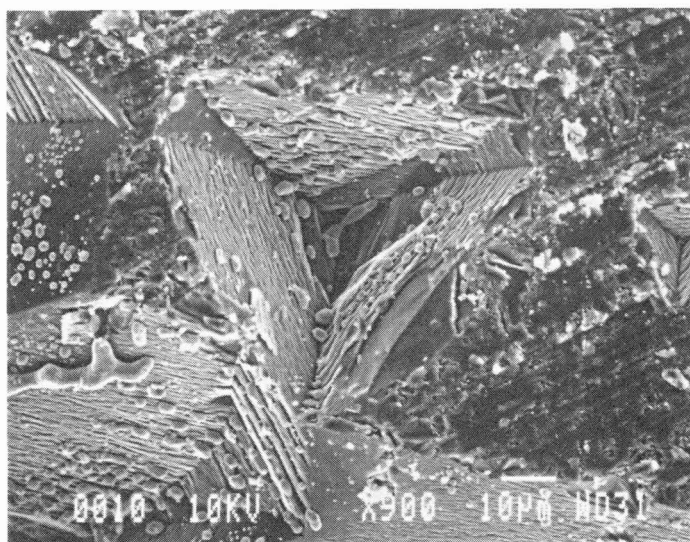
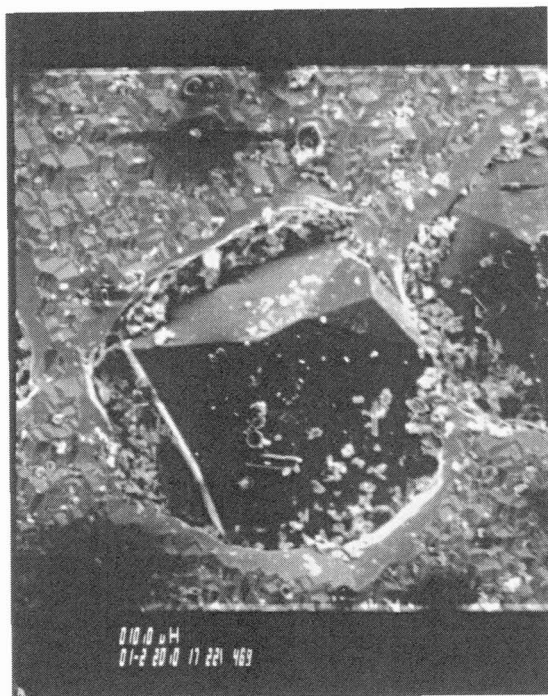


Figure 1 : Inclusion phase in the top and etch-pits in the bottom seen by SEM.

2/ EXPERIMENTAL METHODOLOGY

Solubility limits have been calculated for each run in term of g/l of aqueous solution. The mass of Madagascar α -quartz generally used is close to 3g with a typical size of 1-2 mm for each grain in order to maintain approximately constant the specific area. Experiments have been carried out in high pressure vessels built with refractory alloys with a cone/cone closing system (Fig. 2).

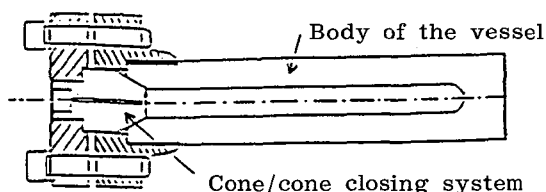


Figure 2 - Diagrammatic section of the high pressure vessel used for dissolution cycles

The reaction vessel, completely filled with the solvent, contains the nutrient placed in a gold tube in order to reduce the inner contamination.

The heating used a conventional furnace. Time (192 hours) is enough, in order to insure that the observed solubility value corresponds to the solubility limit (s_l) in the selected P,T conditions. At the end of the run, the pressure vessel is quenched, the α -quartz removed, dried and reweighed. The mass loss (Δm) is calculated and coupled with the volume of aqueous solution in the vessel (V) leading to the solubility limit value $s_l = \Delta m/V$ correlated to the involved temperature and pressure. To insure the validity of such experiments at least two tests for each (P,T,t) set were carried out.

3/ EXPERIMENTAL RESULTS

3.1/ Pressure effect on α -quartz dissolution at $T \approx 400^\circ\text{C}$ for different solvents NaOH(1M) and $\text{Na}_2\text{CO}_3(1\text{M})$

3.1.1/ α -quartz solubility limit using an aqueous solution NaOH(1M)

The solubility limit values have been plotted versus pressure at 400°C (Fig. 3).

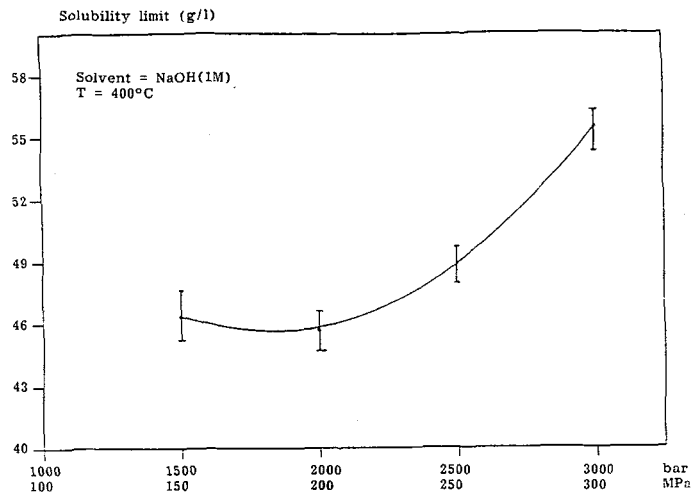


Figure 3 - Quartz solubility limit in NaOH(1M) vs. pressure at constant temperature (400°C)

At pressure below 200 MPa, there is a pressure domain in which the solubility limit (s_l) of α -quartz seems to fall with a minimum (at approximately 200 MPa) with a value close to 45 g/l. At pressure above this, s_l increases in NaOH(1M) up to 300 MPa (last studied experimental pressure). At this upper limit s_l is close to 51.25 g/l.

3.1.2/ α -quartz solubility limit in Na_2CO_3 (1M) aqueous solution

The pressure effect on α -quartz dissolution at constant temperature 400°C $s_l = f(P)$ is given on figure 4.

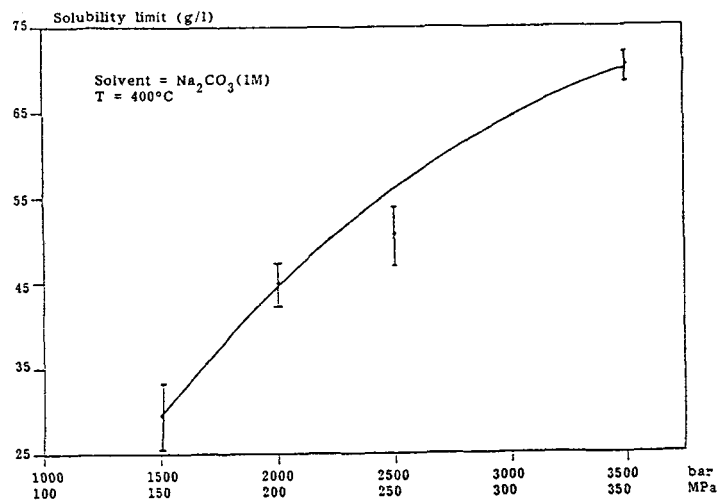


Figure 4 - Quartz solubility limit in Na_2CO_3 (1M) vs. pressure in constant temperature (400°C)

3.2/ Comparison of the solubility limit (s_l) of α -quartz between NaOH(1M) and Na₂CO₃(1M) aqueous solutions vs. pressure at a constant temperature (400°C)

At 400°C, the solubility limit for $P \geq 200$ MPa is higher in Na₂CO₃(1M) than in NaOH(1M) (Fig. 5).

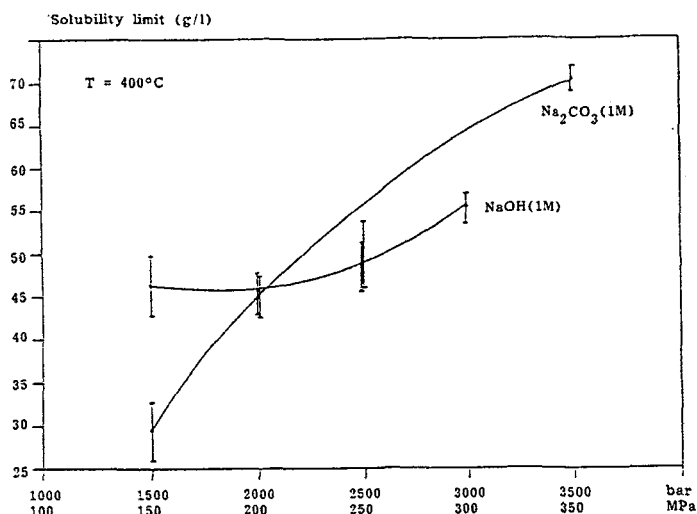


Figure 5 - Solubility limit comparison between NaOH(1M) and Na₂CO₃(1M) vs. pressure at 400°C.

Through these experiments sodium carbonate appears to be a better solvent than sodium hydroxide in high pressure domain for a temperature close to 400°C. This result could be reported in the hydrothermal α -quartz growth applications. Na₂CO₃(1M) solution could be a more appropriate solvent for setting up a high pressure process if the resulting quality of the synthetic quartz is compatible with high frequency applications.

3.3/ Enthalpy of dissolution of α -quartz at constant temperature (400°C)

The data concerning the solubility limit in NaOH(1M) and in Na₂CO₃(1M) aqueous solutions determined by the weight loss method for different pressure values (150-350 MPa) are plotted as $\ln(s_l) = f(1/p)$ (Fig. 6). The corresponding curve is linear in the pressure domain (150-350 MPa)

for $\text{Na}_2\text{CO}_3(1\text{M})$ and presents a small deviation to the linearity for $\text{NaOH}(1\text{M})$ in the domain (200-350MPa).

From the slope of the curves (Fig. 6), the enthalpy values of α -quartz dissolution at constant temperature (400°C) can be calculated versus the nature of the solvent.

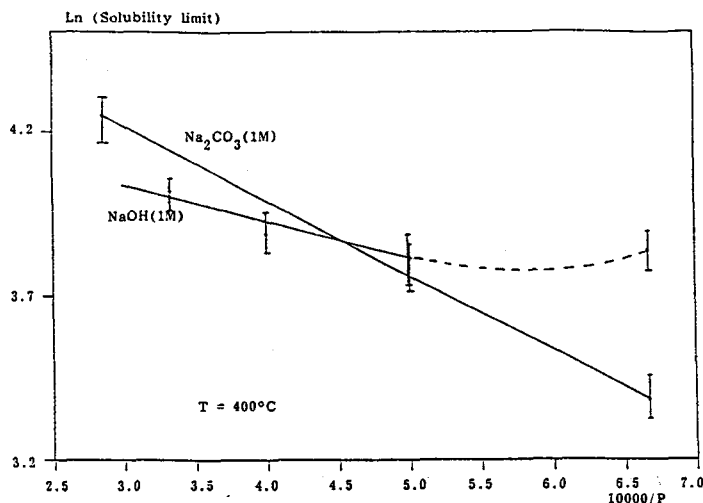


Figure 6 - Logarithm of the solubility (s_1) in $\text{NaOH}(1\text{M})$ and in $\text{Na}_2\text{CO}_3(1\text{M})$ vs. $1/P$

$\Delta H_T = 2395 \pm 5$ cal/mole for $\text{NaOH}(1\text{M})$; $200 \leq P \leq 350$ MPa

$\Delta H_T = 4110 \pm 2$ cal/mole for $\text{Na}_2\text{CO}_3(1\text{M})$; $150 \leq P \leq 350$ MPa

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- [1] Lafon F. Demazeau G., "Pressure effect on the dissolution of α -quartz in different aqueous solutions", High Pressure Research (in press).
- [2] Kennedy George C., Econ. Geol. 45 (1950), 629-653.
- [3] Laudise R.A., Contribution from the bell Tel. Lab., 81, 562-564, 81.