Solvothermal Synthesis of α-Quartz Powder Doped with Germanium

Alain Largeteau, Stéphane Darracq, and Graziella Goglio

Institut de Chimie et de la Matière Condensée de Bordeaux – CNRS, Université Bordeaux1, Site de l’ENSCPB, 87 Avenue du Dr. A. Schweitzer, 33608 PESSAC Cedex, France

Reprint requests to Dr. A. Largeteau. Fax : (+33) 540002761.
E-mail: largeteau@icmcb-bordeaux.cnrs.fr


This work, dedicated to Gérard Demazeau, Emeritus Professor at the University of Bordeaux 1, on the occasion of his 65th birthday, concerns one of the subjects that he studied in the Institute of Condensed Matter Chemistry of Bordeaux (ICMCB-National Centre for Scientific Research). Gérard Demazeau has developed a large number of themes in the field of High Pressure starting, 40 years ago, with Solid State Chemistry. He has worked especially on the stabilization of high oxidation states of transition metals to study the correlations between structure and properties. His research in Materials Science has been devoted to the synthesis of nano- or micro-crystallites and large single crystals for various industrial applications. He has also studied, for 20 years, the pressure effects in Biosciences, in particular in Food Science and in Medicine. His dynamic personality allowed him to publish approximately 500 articles, most of them in high-quality journals.

Experimental investigations concerning the synthesis of Si$_{1-x}$Ge$_x$O$_2$ solid solutions with quartz structure have been carried out under solvothermal conditions from sol-gel preparations. The cell parameters of the powders have been determined by X-ray powder diffraction. The amount of germanium inside the SiO$_2$ structure was measured also by electron probe micro-analysis (EPMA).

**Key words:** Solvothermal Synthesis, α-Quartz, Germanium, X-Ray Diffraction, Sol-Gel Synthesis

Introduction

SiO$_2$ with α-quartz structure is a very well known piezoelectric material [1]. However, to be adapted to the industry needs, its piezoelectric properties must be increased. In order to reach this goal, some oxides such as AlPO$_4$ and GaPO$_4$ have been studied for several years. More recently, new research about α-GeO$_2$ [2–4] has shown that this compound could also be a promising piezoelectric material. Studies were only carried out on bulk crystal growth of α-Si$_{1-x}$Ge$_x$O$_2$, but due to the limited stability domains of α-GeO$_2$ (stable between 1033 °C and 1116 °C), the growth of perfect single crystals by hydrothermal methods is difficult, and the germanium contents are inhomogeneous in the crystals [4, 5]. For that reason, any stoichiometric synthesis of micro- or nano-crystallites of α-Si$_{1-x}$Ge$_x$O$_2$ would improve the knowledge of the physical properties of oxides with α-quartz-type structure and would allow to verify the effect of the replacement of Si atoms by the larger Ge atoms. Actually, few studies about these solid solutions have been reported. The phase equilibrium of the system GeO$_2$–SiO$_2$ [6] was determined up to 1000 °C at 70 MPa from a mixture of α-GeO$_2$ and amorphous SiO$_2$ and by using a hydrothermal process. This study showed that germanium can be incorporated into the α-quartz structure if $x$ is lower than 0.31.

Here, we present our first results concerning the stabilization of an α-Si$_{1-x}$Ge$_x$O$_2$ solid solution with $x$ up to 0.50. A solvothermal process has been used with different amorphous sol-gel phases as precursors in order to strongly improve the chemical reactivity and to prepare crystallites well-defined in size and morphology [7].

Experimental Section

The synthesis of the α-Si$_{1-x}$Ge$_x$O$_2$ solid solutions was performed in two steps: (i) synthesis of a sol-gel from a mixture of alkoxides or acetate and oxide, and (ii) crystallization from the gel in the form of fine particles through a solvothermal treatment.

Two types of sol-gel processes have been investigated. In the first case, tetraethyl-orthogermanate [Ge(OC$_2$H$_5$)$_4$] and tetraethyl-orthosilicate [Si(OC$_2$H$_5$)$_4$] were used as precur-
Precursor (No. synthesis) | Theor. \( x \) | \( T \) (°C) | \( P \) (MPa) | Structure | Lattice constants \( a \) (Å) | \( c \) (Å) | \( c/a \)
--- | --- | --- | --- | --- | --- | --- | ---
Natural quartz | | | | \( \alpha \)-quartz | 4.924(1) | 5.420(1) | 1.101
Amorphous A (1) | 0.10 | 700 | 40 | \( \alpha \)-quartz | 4.916(1) | 5.413(1) | 1.101
Amorphous A (2) | 0.10 | 800 | 100 | \( \alpha \)-quartz | 4.929(1) | 5.433(1) | 1.102
Amorphous A (3) | 0.30 | 800 | 80 | \( \alpha \)-quartz | 4.931(1) | 5.444(1) | 1.104
Amorphous A (4) | 0.40 | 700 | 90 | \( \alpha \)-quartz + amorphous solid | | | |
Amorphous A (5) | 0.50 | 700 | 90 | \( \alpha \)-quartz + GeO\(_2\) | 4.9097(9) | 5.6249(1) | 1.146
Amorphous A (6) | 0.10 | 650 | 85 | \( \alpha \)-quartz + cristobalite | 4.915(2) | 5.415(3) | 1.102
Amorphous A (7) | 0.20 | 700 | 80 | \( \alpha \)-quartz + cristobalite + GeO\(_2\) | 4.907(2) | 5.402(3) | 1.101
Amorphous A (8) | 0.30 | 600 | 150 | \( \alpha \)-quartz | 4.914(1) | 5.404(1) | 1.10
Amorphous B (9) | 0.10 | 700 | 80 | \( \alpha \)-quartz + cristobalite as impurity | | | |
Amorphous B (10) | 0.50 | 700 | 85 | \( \alpha \)-quartz + cristobalite + GeO\(_2\) | 4.907(2) | 5.402(3) | 1.101
Germanium oxide (85-1519 JCPDS) | | | | \( \alpha \)-quartz | 4.9069(9) | 5.6249(1) | 1.146

Table 1. Results obtained with amorphous A or B with \( x < 0.5 \) after solvothermal treatment.

Results and Discussion

Ambient air synthesis

In a first step, the behavior of the amorphous compounds (A and B from sol-gel synthesis) was studied with \( x = 0 \) and 0.10 after a thermal treatment for 3 h at atmospheric pressure. With increasing temperature, the transition from the amorphous phase towards a crystalline powder with cristobalite structure was observed. Whatever amorphous compound was used, for \( x = 0.10 \), the transition is above 800 °C and for \( x = 0 \) this temperature seems to increase to 950 °C. Fig. 1 shows an example of the thermal behavior of the amorphous product A with \( x = 0.1 \).

Solvothermal synthesis

As the \( \alpha \)-quartz structure can not be stabilized under these conditions in air, a solvothermal process was chosen. Upon compression, a densification is always observed for the resulting material. Thereby the \( \alpha \)-quartz structure \( (P3_21, a = 4.9121 \text{ and } c = 5.4044 \text{ Å}) \) which has a smaller volume per unit formula \( (V/Z = 37.67 \text{ Å}^3) \) than the cristobalite structure \( (P4_12_12, a = 4.969 \text{ and } c = 6.9260 \text{ Å}) \) \( (V/Z = 42.81 \text{ Å}^3) \), is favored under pressure. Solvothermal treatments were carried out at different temperatures and pressures with 48 h duration. The results are summarized in Table 1, and an example of an X-ray pattern with refinement for a...
Table 2. x Values from electron probe micro-analysis (EPMA) for $\alpha$-Si$_{1-x}$Ge$_x$O$_2$.

<table>
<thead>
<tr>
<th>No. synthesis (precursor)</th>
<th>Theoretical x</th>
<th>Content Ge x</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (A)</td>
<td>0.10</td>
<td>0.09(1)</td>
</tr>
<tr>
<td>Amorphous A</td>
<td>0.20</td>
<td>0.24(2)</td>
</tr>
<tr>
<td>3 (A)</td>
<td>0.20</td>
<td>0.14(1)</td>
</tr>
<tr>
<td>4 (A)</td>
<td>0.30</td>
<td>0.15(1)</td>
</tr>
<tr>
<td>Amorphous A</td>
<td>0.40</td>
<td>0.49(5)</td>
</tr>
<tr>
<td>5 (A)</td>
<td>0.40</td>
<td>0.26(3)</td>
</tr>
<tr>
<td>Amorphous B</td>
<td>0.10</td>
<td>0.11(1)</td>
</tr>
<tr>
<td>8 (B)</td>
<td>0.10</td>
<td>0.04(1)</td>
</tr>
<tr>
<td>Amorphous B</td>
<td>0.20</td>
<td>0.14(1)</td>
</tr>
<tr>
<td>9 (B)</td>
<td>0.20</td>
<td>0.14(1)</td>
</tr>
</tbody>
</table>

Indeed, with amorphous A, pure well defined compounds can be synthesized for $x$ values up to $x = 0.30$ while above $x = 0.40$ impurities such as germanium dioxide appear.

With amorphous B as soon as $x$ goes past 0.20, it is difficult to stabilize only the $\alpha$-quartz phase. The evolution of the lattice parameters versus the germanium content is slight but significant as shown in Table 1. In order to determine the real compositions of the solid solutions $\alpha$-Si$_{1-x}$Ge$_x$O$_2$, the powders were analyzed by Energy Dispersive X-ray Spectroscopy (Table 2). These values show several trends. First, there is an important loss of germanium on going from the amorphous precursor to the crystallized phase. The stoichiometries of the solid solutions are thus lower than the expected theoretical contents. However, an increase of the germanium content is observed as this element is incorporated in the structure. Actually with these synthesis parameters, the maximum content of Ge to be reached is 25 at-% which is in agreement with the Ge optimized solubility ($x \approx 0.30$) found by Miller et al. [6] for the structure type $\alpha$-quartz.

Conclusion

These first results show that solid solutions Si$_{1-x}$Ge$_x$O$_2$ with the $\alpha$-quartz structure can be stabilized though a solvothermal process using a reactive amorphous precursor. Without a pressure effect, the cristobalite structure is preferentially obtained after thermal treatment. Residual carbon which is present in the final compound must be removed in further steps, in order to study the physico-chemical properties of $\alpha$-Si$_{1-x}$Ge$_x$O$_2$.

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