Solvothermal Synthesis of α-Quartz Powder Doped with Germanium

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Z. Naturforsch. **2008**, *63b,* 739 – 741; received February 4, 2008

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 $Si_{1-x}Ge_xO_2$ 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-$Si_{1-x}Ge_xO_2$, 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-$Si_{1-x}Ge_xO_2$ 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-$Si_{1-x}Ge_xO_2$ 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-$Si_{1-x}Ge_xO_2$ 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 $[Ge(OC_2H_5)_4]$ and tetraethyl-orthosilicate $[Si(OC_2H_5)_4]$ were used as precur-

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

Precursor (No. synthesis)	Theor. x	T (°C)	P (MPa)	Structure	Lattice constants		
					a (Å)	c (Å)	c/a
natural quartz				α-quartz	4.915(1)	5.407(1)	1.100
Amorphous A (1)	0.10	700	40	α-quartz	4.924(1)	5.420(1)	1.101
Amorphous A (2)	0.10	800	100	α-quartz	4.916(1)	5.413(1)	1.101
Amorphous A (3)	0.20	800	100	α-quartz	4.929(1)	5.433(1)	1.102
Amorphous A (4)	0.30	800	80	α-quartz	4.931(1)	5.444(1)	1.104
Amorphous A (5)	0.40	700	90	α-quartz + amorphous solid			
Amorphous A (6)	0.50	700	90	α-quartz + GeO_2			
Amorphous B (7)	0	600	150	α-quartz	4.914(1)	5.404(1)	1.10
Amorphous B (8)	0.10	650	85	α-quartz	4.907(2)	5.402(3)	1.101
Amorphous B (9)	0.20	700	80	α-quartz + cristobalite as impurity	4.915(2)	5.415(3)	1.102
Amorphous B (10)	0.50	700	85	α-quartz + cristobalite + GeO_2			
Germanium oxide (85-1519 JCPDS)				α-quartz	4.9097(9)	5.6249(1)	1.146

sors, respectively. They were dissolved in 2-methoxyethanol with addition of 5 – 10 % of HNO_3 (concentration 65 %) under nitrogen atmosphere and heated at 80 °C with reflux for thirty minutes and then at 150 °C for 1 h in air. The as-obtained material is a yellowish amorphous compound (amorphous A). In the second case [8], silicon tetra-acetate [$C_8H_{12}O_8Si$] and amorphous germanium oxide [GeO_2] were dissolved in a mixture of citric acid and ethylene glycol to form citrate complexes after 1 h at 200 °C. A treatment at 250 °C for 24 h led to a black amorphous polymeric precursor (amorphous B).

These amorphous precursors were put into sealed gold tubes. In addition, residual organic compounds still present in the sol-gel acted as solvent. The tube was set in an autoclave filled with the appropriate amount of water and heated up to 800 °C, with a pressure depending on the temperature.

The structures of the products were investigated by X-ray diffraction (XRD, Philips PW1820, PANalytical X'pert), and lattice parameters were refined with the program FULLPROF. The substitution level was analyzed also by electron probe micro-analysis (EPMA).

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 $x = 0.1$.

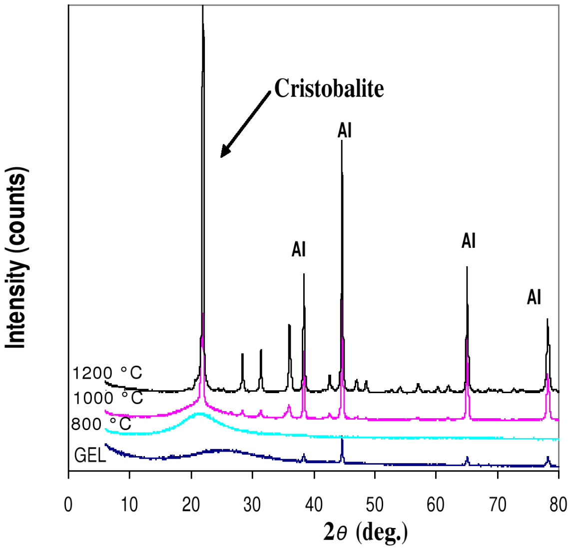

Fig. 1. Powder X-ray diffraction pattern of amorphous A with x = 0.10 after treatment at different temperatures and atmospheric pressure (Al comes from the X-ray analysis support).

Solvothermal synthesis

As the α-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 α-quartz structure ($P3_221$, a = 4.9121 and c = 5.4044 Å) which has a smaller volume per unit formula (V/Z = 37.67 Å^3) than the cristobalite structure ($P4_12_12$, a = 4.969 and c = 6.9260 Å) (V/Z = 42.81 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 α-$Si_{1-x}Ge_xO_2$.

No. synthesis (precursor)	Theoretical x	Content Ge x
1 (A)	0.10	0.09(1)
Amorphous A	0.20	0.24(2)
3 (A)	0.20	0.14(1)
4 (A)	0.30	0.15(1)
Amorphous A	0.40	0.49(5)
5 (A)	0.40	0.26(3)
Amorphous B	0.10	0.11(1)
8 (B)	0.10	0.04(1)
Amorphous B	0.20	0.14(1)
9 (B)	0.20	0.14(1)

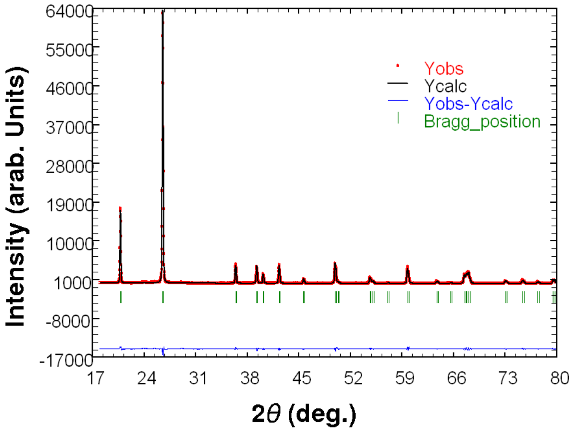

Fig. 2. Powder X-ray diffraction pattern after solvothermal treatment of amorphous A with $x = 0.20$ at 800 °C and 100 MPa.

theorical index $x = 0.20$ is presented in Fig. 2. The resulting powders have a greyish color pointing to the presence of residual carbon from the sol-gel synthesis. Two other results can be observed: first of all, the α-quartz structure can be stabilized under pressure as expected for the two amorphous reagents A and B. Furthermore, it seems that the process with amorphous B, in spite of the fact that it needs a temperature and pressure lower than amorphous A, is less appropriate to obtain α-quartz in pure form.

Indeed, with amorphous A, pure well defined compounds can be synthetized 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 α-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 α-$Si_{1-x}Ge_xO_2$, 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 α-quartz.

Conclusion

These first results show that solid solutions $Si_{1-x}Ge_xO_2$ with the α-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 α-$Si_{1-x}Ge_xO_2$.

Acknowledgement

ISHA (International Solvothermal Hydrothermal Association) is acknowledged for its efforts for promoting solvothermal processes.

[1] F. Lafon, G. Demazeau, *Matériaux et Techniques* **1997**, *3–4*, 11–17; *ibid.* **1997**, *5–6*, 17–24.
[2] E. Philippot, D. Palmier, M. Pintand, A. Goiffon, *J. Solid State Chem.* **1996**, *123*, 1–13.
[3] J. Haines, O. Cambon, E. Philippot, L. Chapon, S. Hull, *J. Solid State Chem.* **2002**, *166*, 434–441.
[4] D. V. Balitsky, V. S. Balitsky, Yu. V. Pisarevsky, E. Philippot, O. Yu. Silvestrova, D. Yu. Pushcharovsky, *Ann. Chim. Sci. Mat.* **2001**, *26*, 183–192.
[5] V. S. Balitsky, D. V. Balitsky, A. N. Nekrasov, L. V. Balitskaya, *J. Phys. IV France* **2005**, *126*, 17–21.
[6] W. S. Miller, F. Dachille, E. C. Shafer, R. Roy, *Am. Mineral.* **1963**, *48*, 1024–1032.
[7] G. Demazeau, *J. Mater. Chem.* **1999**, *9*, 15–18
[8] Y. J. Kwon, K. H. Kim, C. S. Lim, K. B. Shim, *J. Ceram. Proc. Res.* **2002**, *3*, 146–149.