Transformation of MFI to β-Quartz and Coesite under High Pressure and High Temperature

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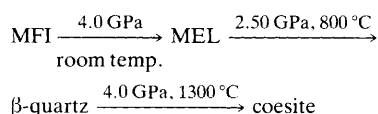[a] Group of Solid State Physics, Jilin University, Changchun 130023, People's Republic of China
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The transformation of MFI to β-quartz, stable at room temperature, and coesite stable under high pressure and high temperature, is observed; the quartz and coesite phases are characterized by X-ray powder diffraction, thermogravimetric analysis and differential thermal analysis.

Zeolites are complex aluminosilicates with three-dimensional framework structures enclosing cavities occupied by ions and water molecules.[1] From the thermodynamic point of view, zeolites are members of unstable phases, as changes of pressure or temperature may transform a particular zeolite into another zeolite or an inorganic salt. The effect of temperature on the stability of zeolites has been widely studied, but there has been little work on the effect of pressure.

Previously we reported for the first time the effect of pressure on the stability of a zeolite.[2] For simplicity we chose to study the all-silicon MFI which has the formula $Si_{96}O_{192} \cdot 16H_2O$. We found that MFI was directly transformed into MEL and that this transformation was irreversible.

In this communication, we further report the effect of pressure and temperature on the stability of MFI. We have found that MFI is transformed into β-quartz, which is obtained for the first time at room temperature, to the best of our knowledge, and coesite under high pressure and high temperature (Scheme 1).

$$\text{MFI} \xrightarrow[\text{room temp.}]{4.0\,\text{GPa}} \text{MEL} \xrightarrow{2.50\,\text{GPa}, 800\,°C}$$

$$\beta\text{-quartz} \xrightarrow{4.0\,\text{GPa}, 1300\,°C} \text{coesite}$$

**Scheme 1** Transformation of MFI under high pressure and high temperature

MFI was synthesized under hydrothermal methods using tetrapropylammonium bromide as the templating agent. Before the high pressure–high temperature experiments, MFI was heated to 200 °C to remove the adsorbed water and water of crystallization. High pressure–high temperature experiments were carried out on belt-type high pressure equipment. MFI was placed in the high pressure chamber and the pressure increased up to expected value, the temperature was then increased up to expected value, too. After 20 min, the samples were quenched to room temperature under high pressure, and the pressure was finally released.

X-Ray powder diffraction (XRD) studies were performed using a Rigaku 12 kW copper rotating-anode X-ray diffractometer with a graphite monochromator. Silica was used as an internal standard, and cell parameters were refined by least-squares. Thermogravimetric–differential thermal analysis (TG–DTA) curves were obtained using a Rigaku CN 8097E thermal analyser at a heating rate of 10 °C min⁻¹ in air.

The X-ray powder diffraction pattern of MFI is shown in Fig. 1(a). Comparison with the XRD data of Jablonski et al.,[8] and Baerlocher[4] shows that the sample is pure MFI without MEL intergrowths. The TG–DTA curves of MFI are given in Fig. 2. MFI is stable up to a temperature of 900 °C under normal pressure, no thermal events occur except that the organic templating agents escape from the straight channels at 365 °C and from the S channels at 435 °C; the organic components escaping from the cavities are burned at 550 °C.[2]

The X-ray powder diffraction pattern of MFI following treatment at a pressure of 2.50 GPa and a temperature of 800 °C is shown in Fig. 1(b). Comparison with the X-ray powder diffraction data of Bassett and Lapham[5] obtained at 625 °C shows that MFI is thoroughly transformed into β-quartz after high pressure–high temperature treatment. The β-quartz synthesized in this paper crystallizes in the hexagonal system with lattice constants $a = b = 0.4996$ nm, $c = 0.5453$ nm, which correspond to average values derived from a least-squares refinement of X-ray powder diffraction data.

Up to now, it has always been thought that the stable room temperature polymorph of SiO_2 is α-quartz, which is transformed to β-quartz on heating above 573 °C. β-Quartz undergoes a phase change to α-quartz during cooling below 573 °C and no matter how fast the cooling rate, the transition cannot be suppressed. The only way to obtain structural information on β-quartz is by X-ray diffraction at high temperature.[6] However, we have found that after high-pressure quenching, β-quartz does not transform into α-quartz below 573 °C. These results can be explained as follows. In both α- and β-quartz the silicon atoms are tetrahedrally coordinated by oxygen. It has been found that the α form is a
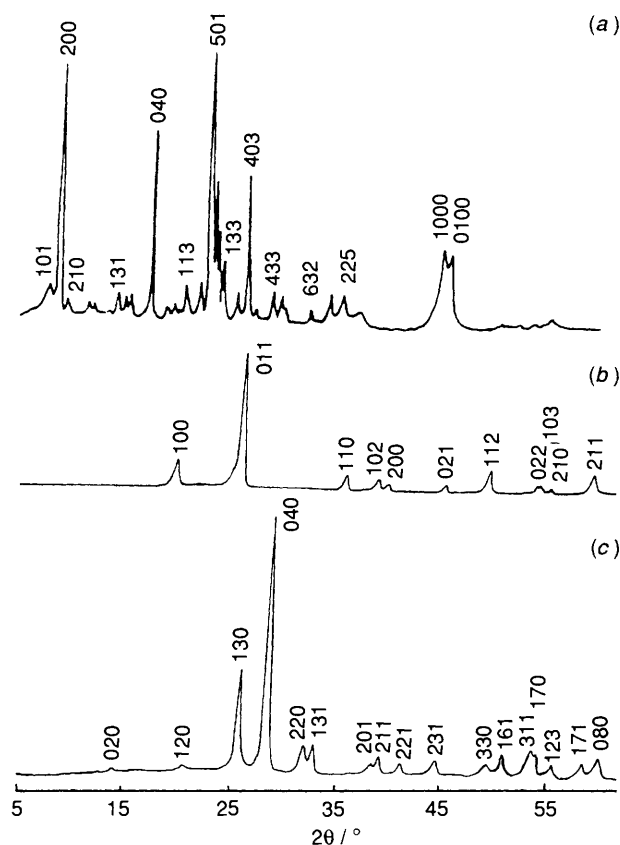
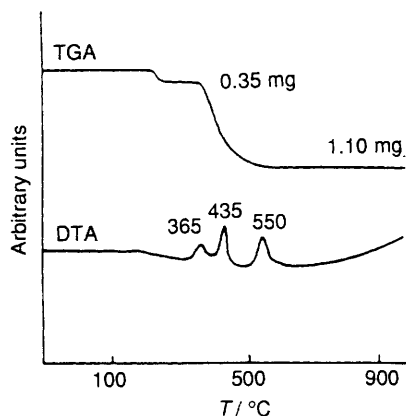**Fig. 1** X-Ray powder diffraction pattern of (a) MFI, (b) β-quartz and (c) coesite

Fig. 2 TG–DTA curves for MFI

distorted version of the β form and that the way in which the tetrahedra are linked together is the same in the two forms. So the transformation from the one to the other can be effected by a small displacement of the silicon atoms without any disturbance of the Si–O bonds. Because the conversion of β → α quartz merely involves a small distortion of the structure without any radical rearrangement and is an easy and reversible process, the β-quartz will not be obtained at room temperature unless the cooling rate is very fast. Quenching samples under high pressure restricts the motion of atoms; using high pressure is equivalent to increasing the cooling rate[7,8] and the cooling rate under high pressure is far faster than that under normal pressure. Although the transformation of β-quartz to α-quartz is very fast under normal conditions, there probably would not be enough time for this transformation during high pressure quenching. The reason why β-quartz had not been obtained in the past is that the the cooling rate under normal pressure is slower than that under high pressure. The fact that β-quartz, which is stable at room temperature is obtained under normal pressure shows that quenching under high pressure can effectively intercept and capture some metastable phases which are difficult to obtain under normal conditions. When the cooling rate is *ca.*

10^2 °C s^{-1} under a pressure of 1–5 GPa, some metastable phases[7–9] can be gained which would usually be obtained at a cooling rate of $10^6 \sim 10^8$ °C s^{-1} under normal pressure.

The X-ray powder diffraction pattern of MFI treated under a pressure of 4.0 GPa and a temperature of 1300 °C is given in Fig. 1(c). With reference to the X-ray powder diffraction data of Zoltai and Buerger,[10] we can confirm that MFI is thoroughly transformed into coesite after following high pressure and high temperature treatment, In the past, the synthesis of coesite was very difficult (3.5 GPa, 1750 °C, 15 h).[11] However, we have shown that the pressure and temperature values for the synthesis of coesite are greatly decreased and it only takes 20 min. The reason is that the MFI can be regarded as a reaction precursor, in which all atoms are well mixed at the atomic scale, thus the activation energy of the reaction will decrease greatly and the synthetic reaction can be carried out under a lower pressure and temperature in a shorter time.

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