LETTER

Structural phase transitions of tridymite: A ^{29}Si MAS NMR investigation

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ABSTRACT

Changes in ^{29}Si MAS NMR spectra of synthetic tridymite from room temperature to 504 °C are consistent with the structural phase transitions previously observed by X-ray diffraction and by optical and calorimetric methods. The results also provide evidence for a disordered or incommensurate structure for the OP and OS phases (stable from about 110 to 200 °C) and for dynamical disordering of the O atoms at greater than kilohertz frequencies for at least the higher temperature OC and HP phases. The time-averaged Si-O-Si bond angles of the OC and HP phases inferred from the ^{29}Si chemical shifts are identical (154.1 ± 1°) and similar to that of β-cristobalite (153.3 ± 1°, Phillips et al., in preparation). The Si-O-Si bond angles for the OS, OC, and HP phases inferred from the NMR data are significantly less than those obtained from the mean atom positions determined by diffraction methods.

INTRODUCTION

Tridymite undergoes a series of at least four structural phase transitions (SPT) between room temperature and ca. 500 °C, but different samples behave differently, and there is considerable controversy about the number of transitions, their temperatures, and the structures of the individual phases (summarized by Kihara, 1978; Nukui et al., 1978; Thompson and Wennemer, 1979; Carpenter and Wennemer, 1985; Smelik and Reeber, 1990; and Graetsch and Flörke, 1991).

We present here a ^{29}Si MAS NMR investigation of the SPTs of tridymite. The ^{29}Si NMR provides information about these SPTs unobtainable by the diffraction, calorimetric, and optical methods used previously because it probes the local rather than average structure.

EXPERIMENTAL METHODS

Samples

We have investigated nine samples of natural and synthetic tridymite but present here NMR data for only two synthetic ones. TEM and XRD examination shows that one is well ordered, monoclinic (MC) tridymite (Sample 6; nomenclature of Nukui et al., 1978) and the other is a mixture of mostly MC grains and some grains with an incommensurate structure (Sample 7). The results are similar for both samples. We illustrate the spectra for only Sample 7 because they have better signal to noise ratios (Fig. 1). The samples used were grown from Na_2WO_4 flux doped with 0.1 wt% $FeCl_3$ (Sample 6) and 0.1 wt% Fe_2O_3 (Sample 7) in a Pt crucible (see Graetsch and Flörke, 1991) at 1400 °C. The Steinbach meteorite tridymite and undoped synthetic samples have T_1 relaxation times too long for practical use in high-temperature NMR experiments.

NMR methods

The ^{29}Si NMR spectra were obtained under magic angle spinning (MAS) conditions at 71.4 MHz ($H_0 = 8.45T$). Spectra from room temperature (RT) to 202 °C were obtained using a modified standard 7-mm MAS probe. Spectra from 155 to 504 °C were obtained using a Doty Scientific high-T MAS probe. The spectra from the high-T probe contain approximately an additional 10-Hz instrumental peak broadening, which does not significantly affect the data interpretation. Based on previous experiments (Phillips et al., in preparation) the temperature accuracy is about ±5 °C and the heterogeneity 3–5 °C.

SPTs OF TRIDYMITE

At room temperature, MC tridymite is monoclinic. At about 100–110 °C it undergoes an SPT to a phase (OP) that most workers believe to be orthorhombic with a superlattice that has a translation 3b compared with high-temperature orthorhombic (OC) tridymite (Kihara, 1977; Nukui et al., 1978; Graetsch and Flörke, 1991). For
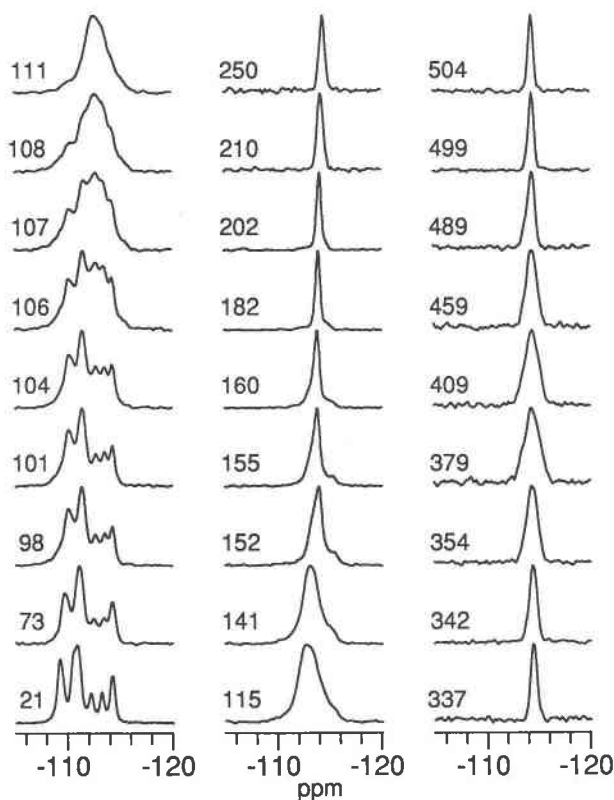
Fig. 1. The ^{29}Si MAS NMR spectra of synthetic tridymite (Sample 7) from 21 to 504 °C. Spectra at 202 °C and below were obtained using a modified, standard Doty Scientific MAS probe; spectra at 210 °C and above were collected using a Doty Scientific high-T MAS probe.

Fig. 2. Temperature variation of the second moments (a measure of peak breadth) of the ^{29}Si MAS NMR spectra of synthetic tridymite.

Steinbach tridymite, Dollase (1967) reported without supporting evidence an incommensurate superstructure in this temperature range.

Most studies of synthetic MC tridymite show that the OP phase undergoes an SPT at about 150–180 °C to another orthorhombic phase (OS), which Nukui et al. (1978) reported to have an incommensurate structure. At about 190 °C the OS phase undergoes a transition to an orthorhombic phase (OC) that yields diffuse streaks in single-crystal XRD photographs (Dollase, 1967; Nukui et al., 1978). This phase contains one Si site. The MC to OP, OP to OS, and OS to OC transitions all yield heat capacity anomalies in differential scanning calorimetry (DSC) data (Thompson and Wennemer, 1979). There is also a less well understood transition at about 350–400 °C from the OC phase to a hexagonal phase (HP, Kihara, 1978). This SPT does not yield an unambiguous signal in the DSC data (Thompson and Wennemer, 1979).

NMR RESULTS

The NMR spectra of our tridymite samples (Fig. 1) show dramatic changes that reflect the structural changes that occur with increasing temperature. The RT spectrum is similar to but slightly better resolved than the one reported by Smith and Blackwell (1983). The five peaks
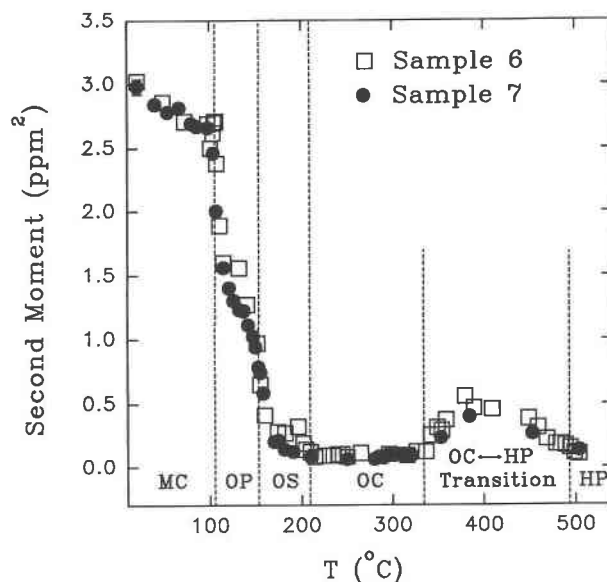
(one slightly split) have intensity ratios of essentially 3:5:1:1:2, caused by the overlap of signal from Si on the 12 tetrahedral sites of MC tridymite (e.g., Baur, 1977). With increasing temperature up to about 98 °C, the only change is a shifting of the peaks by, at most, 0.5 ppm to more negative values and a decrease in resolution due to a slight increase in peak width and decrease in peak separation.

The transition to OP begins at about 101 °C, with the appearance of additional intensity in the −112 to −115 ppm range, and at 115 °C all vestiges of the peaks for the low-temperature phase are gone. At this temperature the spectrum consists of a broad, asymmetric envelope and a small shoulder. The first moment (mean chemical shift, not shown) becomes more negative with increasing temperature, and the second moment (a measure of peak width) decreases (Fig. 2).

The OP to OS transition at about 150 °C is marked by a sharpening of this peak and a reduction in the rate of change of the first and second moments with temperature. The small shoulder at more negative chemical shifts remains.

The temperature of the OS to OC transition is difficult to determine precisely (as with the XRD data; e.g., Nukui et al., 1978) but occurs near 200 °C, as marked by the loss of the shoulders and a continuous change of the first moment and peak maximum to −114.4 ppm.

The onset of the OC to HP transition is apparently marked by peak broadening at about 340 °C (Fig. 2). The maximum width occurs at about 380 °C, near the temperature of the OC to HP transition reported by Kihara (1978). Above this temperature the peak progressively narrows, and at 504 °C it is identical to the peak for the OC phase (chemical shift = −114.4 ppm). The first mo-

ment remains within experimental error of this value throughout the temperature range with broadened peaks.

With decreasing temperature (data not shown) the spectra are similar to those obtained with increasing temperature, but there is significant hysteresis. The broadened peaks at the HP to OC transition occur between 390 and 310 °C. The OS phase first appears at 180 °C. The OP phase first occurs at 142 °C. The MC phase first occurs at 77 °C, in agreement with the observations of Nukui et al. (1978).

DISCUSSION

The observed NMR spectra for these two tridymite samples are consistent with the presence of the four SPTs previously reported for reasonably well-ordered synthetic tridymite. For some of the phases the average Si-O-Si angle inferred from the ^{29}Si chemical shifts is significantly different from that obtained from the mean atom positions in structure refinements, as also observed for β-cristobalite (Spearing et al., 1992; Phillips et al., in preparation).

HP and OC tridymite

The single narrow NMR peaks for the HP and OC phases are consistent with the single Si sites of their average structures (Dollase, 1967; Kihara, 1978; Kihara et al., 1986a, 1986b). The problems in comparing the NMR results and the structure refinements have to do primarily with the location of the O atoms. The mean positions of the O atoms in the HP phase lie directly between the Si atoms, forming apparent Si-O-Si bond angles of 180°, the same situation as in β-cristobalite (Peacor, 1973; Wright and Leadbetter, 1975). For OC and HP tridymite and β-cristobalite the thermal ellipsoids for the O atoms are large and anisotropic, and the average Si-O-Si angles may not coincide with the angle between their mean positions (Dollase, 1967; Kihara et al., 1986a, 1986b). A split O-position model for the HP phase gives a mean Si-O-Si angle of 149.2° (Kihara, 1978). For OC tridymite at 220 °C, Kihara et al. (1986a) determined a mean Si-O-Si bond angle of 168.0°, uncorrected for disorder and thermal vibration.

For both HP and OC tridymite, the ^{29}Si chemical shifts are −114.4 ± 0.1 ppm, implying an average Si-O-Si bond angle of 154.1 ± 1° for both phases (Smith and Blackwell, 1983; see Pettifer et al., 1988). For comparison, the chemical shift of −113.9 ppm for β-cristobalite implies an average Si-O-Si bond angle of 153.3 ± 1° (Phillips et al., in preparation). These bond angles assume a linear correlation between the bond angle and the chemical shift for SiO₂ phases. The similarity between the intertetrahedral bond angles of OC and HP tridymite and β-cristobalite is to be expected because their densities and unit-cell dimensions are nearly identical above about 270 °C (Graetsch and Flörke, 1991). With the assumption of equal Si-O distances for both phases, the slightly lower density (ca. 0.01 g/cm³) and slightly longer c-axis dimension (ca.

0.02 Å) for tridymite are consistent with its having a slightly larger time-averaged mean Si-O-Si bond angle than cristobalite, as determined from the NMR chemical shifts.

On the basis of NMR results for the cristobalite polymorphs of AlPO₄ and SiO₂, Phillips et al. (in preparation) concluded that the O atoms in β-cristobalite are dynamically disordered at frequencies greater than about 1 MHz and that this averaging of the O positions is coherent. The ^{29}Si MAS NMR peaks for OC and HP tridymite are narrow, the electron probability density functions of their O sites are very diffuse (Kihara et al., 1986b), and diffraction patterns show diffuse streaking (e.g., Nukui et al., 1978). Thus, it is likely that similar dynamical processes also operate in these phases. Possible processes include rapid fluctuation between twin-related domains (e.g., Hatch and Ghose, 1991) or cooperative tetrahedral motion (e.g., Hua et al., 1988). As for cristobalite, the discrepancies between the tridymite Si-O-Si bond angles obtained from NMR and structure refinements are likely to be due to difficulties in refining diffraction data for dynamically disordered phases in which the time-averaged atomic positions do not correspond to the spatially averaged positions. The broadening of the NMR peaks for tridymite in the temperature range of 340–490 °C indicates the presence of some disorder in the Si-O-Si bond angles that is unaveraged at frequencies greater than about 1 kHz. Such disorder could be due to the presence of strain near the boundaries between the small domains expected at hexagonal to orthorhombic transitions (e.g., Kim et al., 1992).

OP and OS tridymite

The structures of tridymite in the temperature range of the OP and OS phases (ca. 100–200 °C) remain controversial. Neither of these phases yields well-resolved NMR peaks, consistent with the incommensurate modulated structure of OS (Nukui et al., 1978) but inconsistent with a simple, well-ordered structure containing six Si sites (Kihara, 1977). A phase with an incommensurate structure is likely to contain a continuum of Si-O-Si bond angles and yield an NMR spectrum containing a broad envelope of intensity with sharp peaks at singularities in the spectral density (e.g., Phillips et al., 1991). The details of the spectra depend on the dimension and symmetry of the modulation with respect to the underlying lattice (Blinc, 1981). Our spectra are, thus, qualitatively consistent with an incommensurate structure over the entire temperature interval of the OP and OS phases, as proposed by Dollase (1967). However, using NMR alone it is difficult to distinguish an incommensurate structure from the large commensurate superstructure proposed for the OP phase (Kihara, 1977; Nukui et al., 1978).

The mean Si-O-Si bond angle of 157.3° obtained at 155 °C from single-crystal XRD (Kihara, 1977) is also inconsistent with the observed ^{29}Si first moment of −113.7 ppm at this temperature (inferred mean Si-O-Si bond angle = 153.0 ± 1°). Possible explanations of this discrep-

ancy are that there is some dynamical disorder at this temperature or that the incommensurate modulation causes some difficulty in refinement of the structure with diffraction data.

Room temperature tridymite

As shown by Smith and Blackwell (1983), the grand mean Si-O-Si bond angle (150.0°) and the mean ^{29}Si NMR chemical shift (-111.2 ppm) agree reasonably well with the observed correlation of these parameters for all silica polymorphs. For an assignment of the 12 sites and NMR peaks based strictly on mean Si-O-Si bond angle per tetrahedron (Baur, 1977), points for most of these sites also fall within experimental error of a linear correlation. The points for the two Si sites involved in the unusual 179.1° Si-O-Si linkage, however, fall away from such a correlation. Possible explanations for this discrepancy include failure of the linear correlation at these large bond angles or some difficulty with the structure refinements, including possible disorder at the O position in this linkage.

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