Ambient temperature phase transitions in Synthetic Tridymites

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Abstract

New DTA and DSC measurements on synthetic tridymites prepared with the addition of alkali-carbonate, indicated that progressively more disordered tridymites contain more structural units of cristobalite and confirmed the occurrence of a previously reported transition near 337 K at 1 atmosphere. It is unlikely that this represents a transition from MC (one monoclinic form) to PO (pseudo-orthorhombic form) as this interpretation would be inconsistent with the observed transition from MC to PO at 5 ± 1.5 kbar, room temperature (NUKUI et al., 1980). The observed transition at 337 K, 1 atmosphere, could represent the change from MX-1 (another monoclinic form) to PO. Synthetic tridymites prepared with the addition of alkali-tungstate contained large numbers of cristobalite crystals. DSC scans did not reveal on those as well as two natural (terrestrial) tridymites the transition at 337 K, 1 atmosphere.

Keywords: tridymite, phase transition, differential thermal analysis, differential scanning calorimetry, heat-capacity.

INTRODUCTION

The differential scanning calorimeter (DSC) study on various synthetic tridymites by THOMPSON and WENNEMER (1979, Figure 1) covered the temperature range 360 to 770 or 840 K, at 1 atmosphere. Their heat-capacity data above 360 K could not easily be extrapolated to the low temperature (54 to 295 K) results of ANDERSON (1936). That the C_p-T offset between the two data sets of C_p-T data could conceal additional tridymite transitions is clearly the case in view of the observations by HILL and ROY (1958, p. 506) and SATO (1965, 3, p. 219) who reported a further transition at 337 K or 333 to 348 K, respectively. Up to now this transition had only been observed by x-ray methods and the

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question was, whether or not it was associated with a thermal effect and hence, whether it could be detected in the more sensitive DSC-measurements.

As a result of discussions at a Tridymite Workshop in Bochum, January 1983, there is no doubt that several distinct forms of tridymite exist at ambient conditions: the monoclinic MC-type, a monoclinic form called MX-1 by NUKUI and NAKAZAWA (1980, b) identical to S1 of SATO (1964), different members of the PO-family, and finally the triclinic F1-tridymite (KONNERT and APPLEMAN, 1978) but the transitional relationships between the different low-temperature forms are not clear.

A comparison of the HP- (WYCKOFF, 1925) and F1-structure reveals, that a relation similar to that between a-β-cristobalite (WENNEMER and THOMPSON, 1984, Figure 1, C1 to C2), or high and low quartz also exists between these two tridymite structures. Low cristobalite consists of the smaller O-rings as does the triclinic tridymite (F1), while the larger D-rings are characteristic of high-temperature cristobalite. KONNERT and APPLEMAN (1978, p. 402) also pointed out that with regard to its ring shapes, F1 could represent a lower temperature form than for example MC. Therefore a high-low inversion between these two tridymite structures is likely and hence DSC-measurements to liquid nitrogen temperatures were carried out to investigate the possibility of further transitions.

To answer questions concerning the effect of structural order, preparation history and impurity content on the transformations, additional samples for thermal investigations of the transition behaviour were prepared from different starting materials and under various preparation conditions (temperature and heating time). These samples covered a large range of structural mixtures between pure tridymite and pure cristobalite.

PREPARATION AND CHARACTERIZATION OF THE NEW SAMPLES

To obtain more material of the Trid-G4-type (THOMPSON and WENNEMER, 1979, p. 1019) a new batch of the same composition (silica gel plus K_2CO_3) was prepared and heat-treated the same way as before. Cristobalite reflections and diffuse rings in the X-ray powder photograph revealed that the new sample was less ordered than the previous Trid-G4 sample. According to FLOERKE (1967, p. 193, FLOERKE and LANGER, 1972, sample T-1sa) a longer heat treatment increases the long range order of tridymite by decreasing the amount of cristobalite three-layer-units. Consequently different time/temperature runs were performed on several starting mixtures. The samples having the best indication of long-range tridymite order were TR-III' and TR-IV, heated at 1200°C for 161 and 112 hours, respectively. Comparison of these samples with the so-called "standard-tridymite" T-1sa (kindly supplied by O. W. Floerke) by x-ray powder

photographs and DSC-scans revealed that TR-III' was more ordered (defined in the proportion of two-layer-units) while TR-IV was less ordered than Trid-G4.

To obtain information about the effect of different alkalies in the starting materials on the transition behaviour, Li-TR, K-TR and Na-TR were prepared from quartz-powder and Li_2WO_4, K_2WO_4 and Na_2WO_4 (1:1 by weight). After 87 hours, 22 days and 8 days, respectively, and purifying the samples as described by FLOERKE and LANGER (1972, p. 223), but without the final heating at 1400 °C, three tridymites of different alkali type were prepared for DSC measurements. A further characterization of all the samples except TR-800 was achieved in the course of the transmission electron microscope (TEM)-investigations by CARPENTER and WENNEMER (1985). On the basis of the classification given by HILL and ROY (1958) and refined by SATO (1963, a) T-1sa, TR-III', TR-G4 and TR-IV represent S-(stable)-type tridymites, which, according to FLOERKE (1961, p. 91) may be correlated to O-(ordered) tridymite, and, as reported at the Tridymite Workshop (Bochum, January, 1983) correspond to MC-tridymite. Na-TR was found to belong to the MS-type (intermediate between metastable and stable) and Li- and K-TR were revealed to be M-(metastable)-tridymites (which can be compared to D-(discordered)-tridymite of Floerke). A similar classification of TR-G3 was not possible because of the deviation of its x-ray powder diagram from that of the other tridymites and the presence of cristobalite reflections. CR-1 proved to be pure cristobalite. The characterization could be further completed by the determination of the degree of stacking disorder parallel to the c-axes by means of the TEM-investigation. In several cases, cristobalite was identified besides tridymite.

A summary of data from all samples used for thermal-measurements is given in Table 1 which includes classifications according to FLOERKE, SATO and the latest structural work done on tridymite.

DSC RESULTS ON THE SYNTHETIC TRIDYMITE SAMPLES

For comparison with the previous C_p-T measurements on synthetic tridymite, DSC scans were made on T-1sa, TR-III' and TR-IV as well as on Li-, Na- and K-tridymites from 360 to 550 K. In accordance with the observations of FLOERKE and LANGER (1972, p. 223), T-1sa showed two transitions. The first larger peak appeared at 386 K, a few degrees above that reported by FLOERKE and LANGER, while the second smaller peak was at the same temperature that they found (432 K). No further transitions were detected in the 340 to 550 K range. These results agree with the observations by FENNER (1913, p. 373) and TOOL and INSLEY (1938, p. 757).

Table 1 Characterization of the samples investigated by DSC and DTA.

| sample	composition of starting mixture	treatment	cell constants [Å], [°]	impurities	classification FLOERKE (1961)	classification ROY (1958) SATO (1963)	classification NUKUI (1980)
Tl-sa	silica gel : Na_2WO_4	3 d/ 1400°C, purified then 1 d/ 1400°C	a= 5.007 b= 8.600 c= 8.217 α= 91.50	0.012 wt% Na	"O"	S	MC MX-1
TR-III'	silica gel + 1 mol% K_2CO_3	161 h/ 1200°C			O	S	MC MX-1
TR-G4	silica gel + 1 mol% K_2CO_3	12 h/ 750°C 15 h/ 800°C 20 h/ 800°C 20 h/ 900°C 20 h/ 1000°C	a= 8.22 b= 8.60 c= 5.01 γ= 91.5	1.29 wt% K_2O 0.23 wt% Na_2O	O	S	MC MX-1
TR-IV	silica gel + 1 mol% K_2CO_3	112 h/ 1200°C			O	S	MC MX-1
TR-800	silica gel + 1 mol% K_2CO_3	12 h/ 750°C 15 h/ 800°C 20 h/ 800°C	a= 12.99 b= 10.60 c= 12.69 α= 90.5	1.38 wt% K_2O 0.29 wt% Na_2O			
TR-G3	silica gel + 1 mol% Na_2CO_3	12 h/ 750°C 15 h/ 800°C 20 h/ 800°C 20 h/ 900°C 20 h/ 1000°C	a= 13.32 b= 11.03 c= 12.25 γ= 95.1	0.14 wt% K_2O 1.49 wt% Na_2O		? strong cristobalite reflections	?
Li-TR	quartz powder : Li_2WO_4 = 1 : 1	87 h/ 1100°C purified			D	M some cristobalite reflections	PO ?
Na-TR	quartz powder : Na_2WO_4 = 1 : 1	8 d/ 1100°C purified			D – O	MS	
K-TR	quartz powder : K_2WO_4 = 1 : 1	22 d/ 1100°C purified			D	M some cristobalite reflections	PO ?
CR-1	silica gel	20 h/ 1500°C				cristobalite	
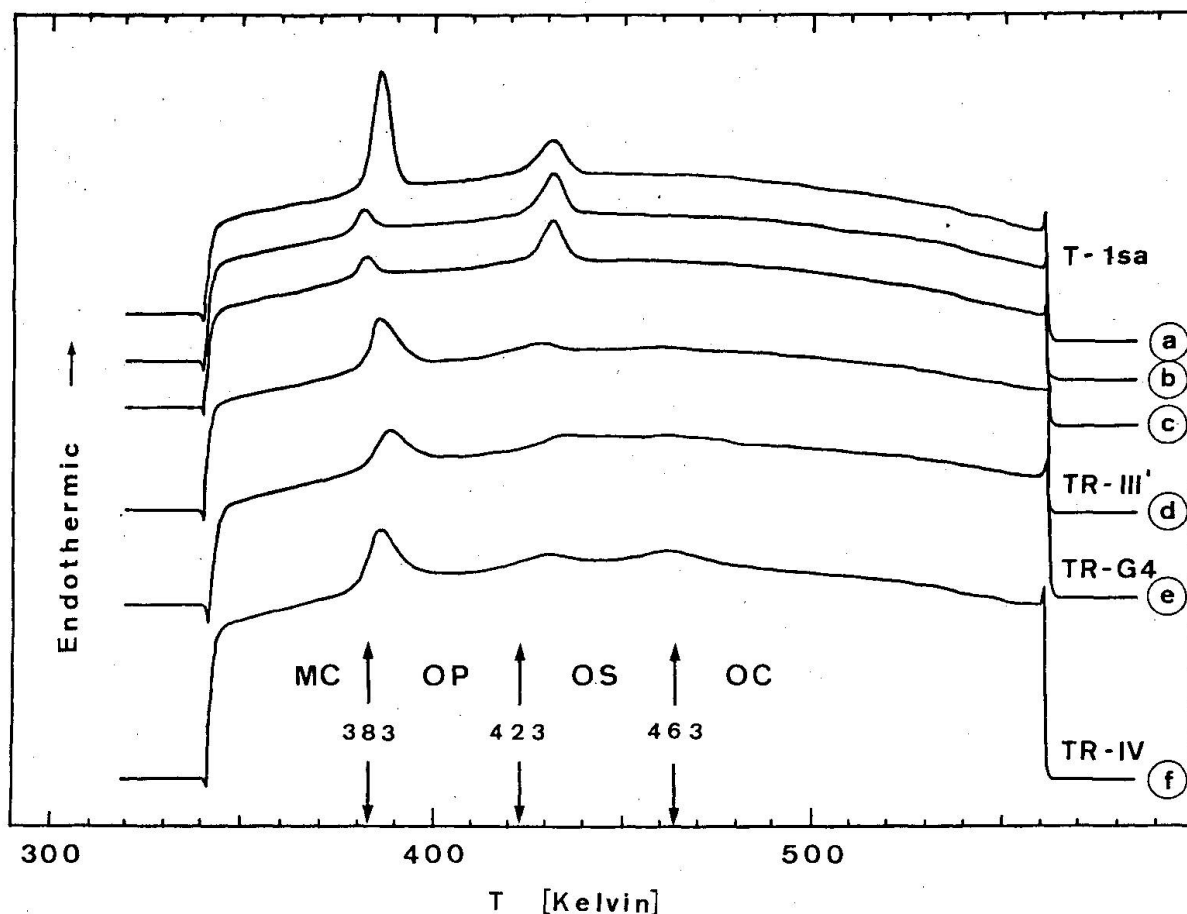
Figure 1 Tracings of Perkin-Elmer DSC-2 scans for various tridymite samples between 340 and 560 K. Scans were made at 10 K min⁻¹, range setting of 5 mcal min⁻¹ cm⁻¹ , chart range 10 mV (= 25 cm) and chart speed 10 mm min⁻¹. Sample weights were about 20 mg for T-1sa, TR-III' and TR-G4, respectively and 26 mg for TR-IV in gold pans of about 200 mg. Scans a, b and c represent successive heatings on T-1sa. The scans d, e and f are first heating-scans on samples TR-III', TR-G4 (Thompson and Wennemer, 1979) and TR-IV, respectively. Nomenclature of polymorphs and temperatures of transition presented by Nukui et al. (1978, Figure 9) are shown.

An immediate reheating of the T-1sa sample gave a surprising result (Figure 1, b). The temperature of the first transition was now 4 K lower (at 382 K) and decreased in intensity from the first scan, whereas the temperature of the second peak was the same, but with the intensity increased. This pattern now remained constant through three further repeated heating cycles. A confirmation of these observations was obtained by DSC-scans on a second sample of T-1sa, which in contrast to the first had not been ground to eliminate an influence of grainsize. These results agree with the repeated thermal cycling of tridymite samples by COHEN and KLEMENT (1980, p. 402, also a sample of FLOERKE T-1sa) although FLOERKE and LANGER (1972, p. 223) did not report any changes in the transition behaviour of T-1sa. There certainly appear to be some structural differences between T-1sa as revealed by the TEM-investigations (CARPENTER and WENNEMER, 1985) and MC from the literature. By beam-

heating with the TEM, T-1sa and the other samples could be taken above their transition temperature to give a hexagonal high-temperature form. On cooling, T-1sa invariably transformed to give a superlattice definitely different from the original one. The same result was obtained for all those samples which according to their superlattice were similar to T-1sa. On the other hand, the transformation of this second structure was fully reversible. The TEM-observations compare quite well with the interpretation of the DSC-results.

According to J. LOENS (Tridymite Workshop), the change in transition behaviour of T-1sa could perhaps be taken as a hint to metastable existence of a high-temperature form (may be OP) down to room temperature. A confirmation of this explanation comes from the observation of a "recovery of the transition behaviour" after less than two months (see below), the immediate "recovery" after supercooling to liquid nitrogen temperature (see below) and the observation of COHEN and KLEMENT (1980, p. 402) that annealing at about 333 K for one hour has the same effect.

On the basis of the characterization (Table 1) the degree of order in TR-III' and TR-G4 is the same. Thus a similar transition behaviour with respect to temperature and intensity of the effects could be expected for these two samples, and was indeed seen (Figure 1). The first transition in TR-IV is at 386 K, the same temperature as was found for T-1sa. A broad and rather weak effect could be seen at 430 K and a third one at 463 K. As the third peak is quite large compared to the second one, TR-IV proved to be less ordered than TR-III' or even Trid-G4 where this peak has been related to the a-β-cristobalite inversion. So, as a result of the characterization given in Table 1 and confirmed by the DSC-measurements, a sequence of increasing order—that is increasing number of two layer units—was revealed from TR-IV through TR-G4 through TR-III' to T-1sa with a consequent decrease in the amount of cristobalite units.

Although the newly prepared samples provide us with useful DSC-data on tridymites with fewer cristobalite layers in the same temperature range as previously investigated (360 to above 550 K), we still face the problem of possible further transitions between 360 and 295 K, especially as HILL and ROY (1958, p. 506) and SATO (1964, p. 219) have already reported transitions in this region. It was possible to study the new tridymite samples between 140 and 620 K by means of a Mettler DTA 2000 (courtesy Dr. Wiedemann, Mettler Instruments, Greifensee).

DTA RESULTS ON OLD AND NEW SYNTHETIC TRIDYMITE SAMPLES FROM 140 TO 620 K

The results of the temperature scans made with the Mettler DTA 2000 are shown in Figure 2 and include runs made on remaining lots of the materials previously measured with the DSC. Because only 7 mg of the original Trid-G4
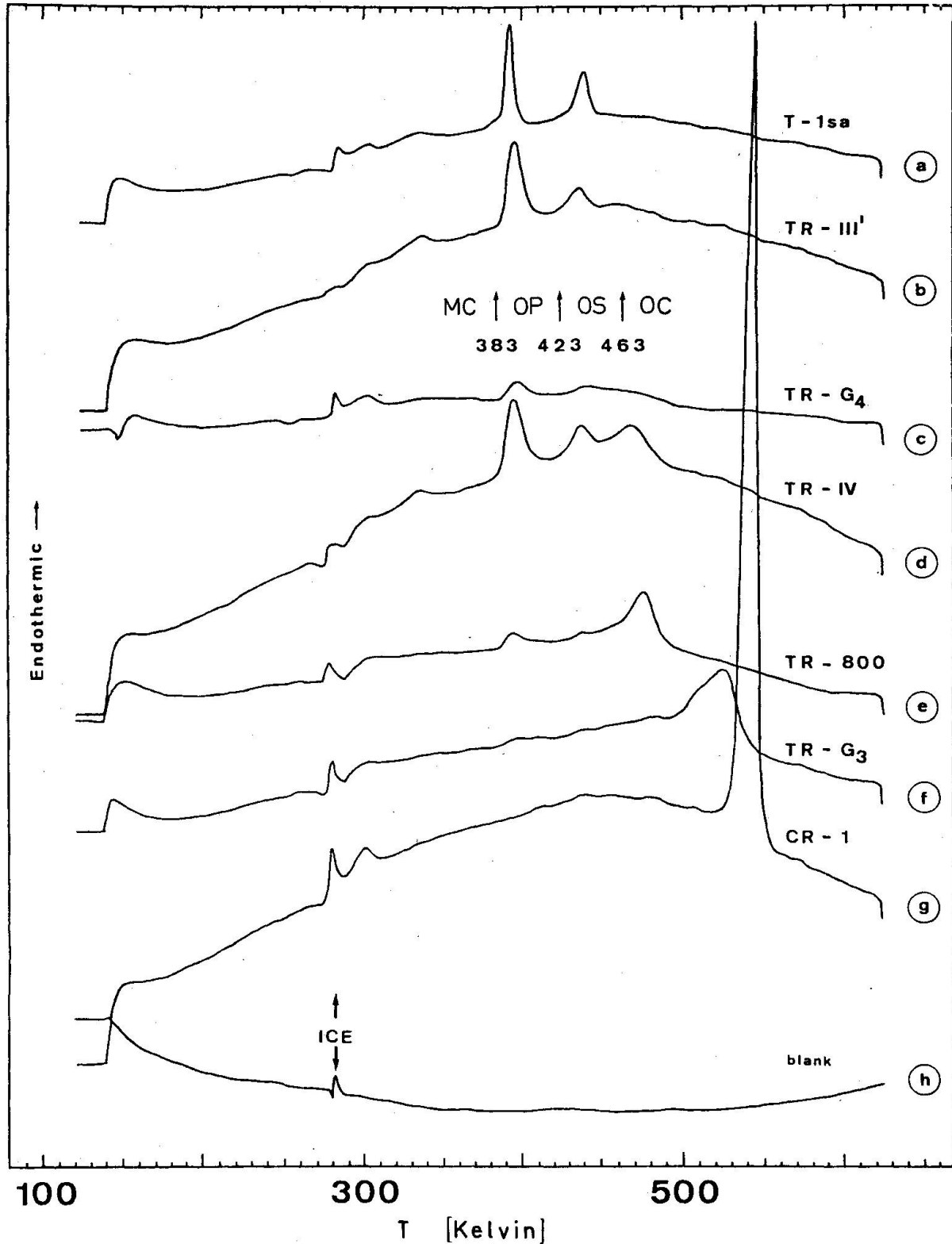
Figure 2   Traces of Mettler DTA 2000 scans for various synthetic samples of tridymite and cristobalite and an empty pan (blank) between 140 and 620 K. Scans were made at 8 K min⁻¹, range setting of 100 mμV and chart speed of 5 mm min⁻¹ were used. For TR-G4 only 7 mg were available and for the others about 25 mg. Aluminum pans of about 50 mg were used. Liquid nitrogen was used as the cooling medium. The same transitions were observed as with the DSC above 380 K with the observation of new peaks below this. The peak at about 280 K is due to ice melting, the peak near 300 K for the tridymites occurred also in the Al_2O_3-standard (not shown) and in the cristobalite. The peak at 336 K is considered to be an inversion in tridymite (see also HILL and ROY, 1958, p. 507 and SATO, 1963, p. 222). Nomenclature as in Figure 1.

material were left the DTA-peaks are much smaller than for the other samples when 15 to 30 mg were used. The peaks corresponding to the transitions obtained with the DTA show good agreement in temperature, peakshape, and intensity compared to the DSC measurements but the C_p-determination with the DTA was less satisfactory and consequently the C_p-T values are not given.

Although the sample T-1sa was repeatedly cycled on the DTA from liquid nitrogen temperature (actually beginning heating at 138 K) to 620 K, neither the temperature nor the intensity of the transitions changed, compared to the results shown in Figure 1 for the DSC-scans on T-1sa. For all other samples the DSC and DTA results showed excellent agreement in the ranges of temperature overlap. Of particular interest in the DTA scans was the appearance of new peaks below 360 K.

FURTHER DSC RESULTS ON TRIDYMITE T-1sa

As the only significant difference between the DSC- and the DTA-measurements was the scan starting-temperature (360 K and 138 K, respectively), the influence of low temperature annealing on the transition behaviour of T-1sa was investigated systematically. After an interval of 14 months further measurements were performed on T-1sa (Figure 3, b) revealing that the trace was nearly identical to that of the first heating, that is T-1sa had "recovered its transition behaviour". However on successive cooling (Figure 3, c), it showed the same change in peak intensity as described above. The sample was then held in liquid nitrogen for about one minute, heated again (Figure 3, d) and once more the transition peaks were analogous to the original ones. Repeated cooling and heating between 340 and 450 K (Figure 3, e and f) gave the same changes as observed previously. The time required for "recovery" of T-1sa is less than two months as proved by DSC-measurements on a new and more sensitive Perkin-Elmer DSC-2C (courtesy of H. Arend, Inst. Solid State Physics, ETH Zurich) several days later (Figure 3, g). From these measurements the 337 K transition could be detected very clearly and the large peak which was at 391 K was now revealed to have an additional shoulder at about 380 K.

DSC RESULTS ON SYNTHETIC ALKALI-WO$_4$-TRIDYMITES

The DSC heating results on the synthetic alkali-WO$_4$-fluxed samples are shown in Figure 4. The features of Li-TR (Figure 4, a) and Na-TR (Figure 4, b) showed a similarity to the traces of repeatedly heated T-1sa and did not change with successive heatings. Unlike the behaviour of T-1sa, the peak intensity of the WO$_4$-tridymites was not influenced by the procedure of cooling in liquid ni-
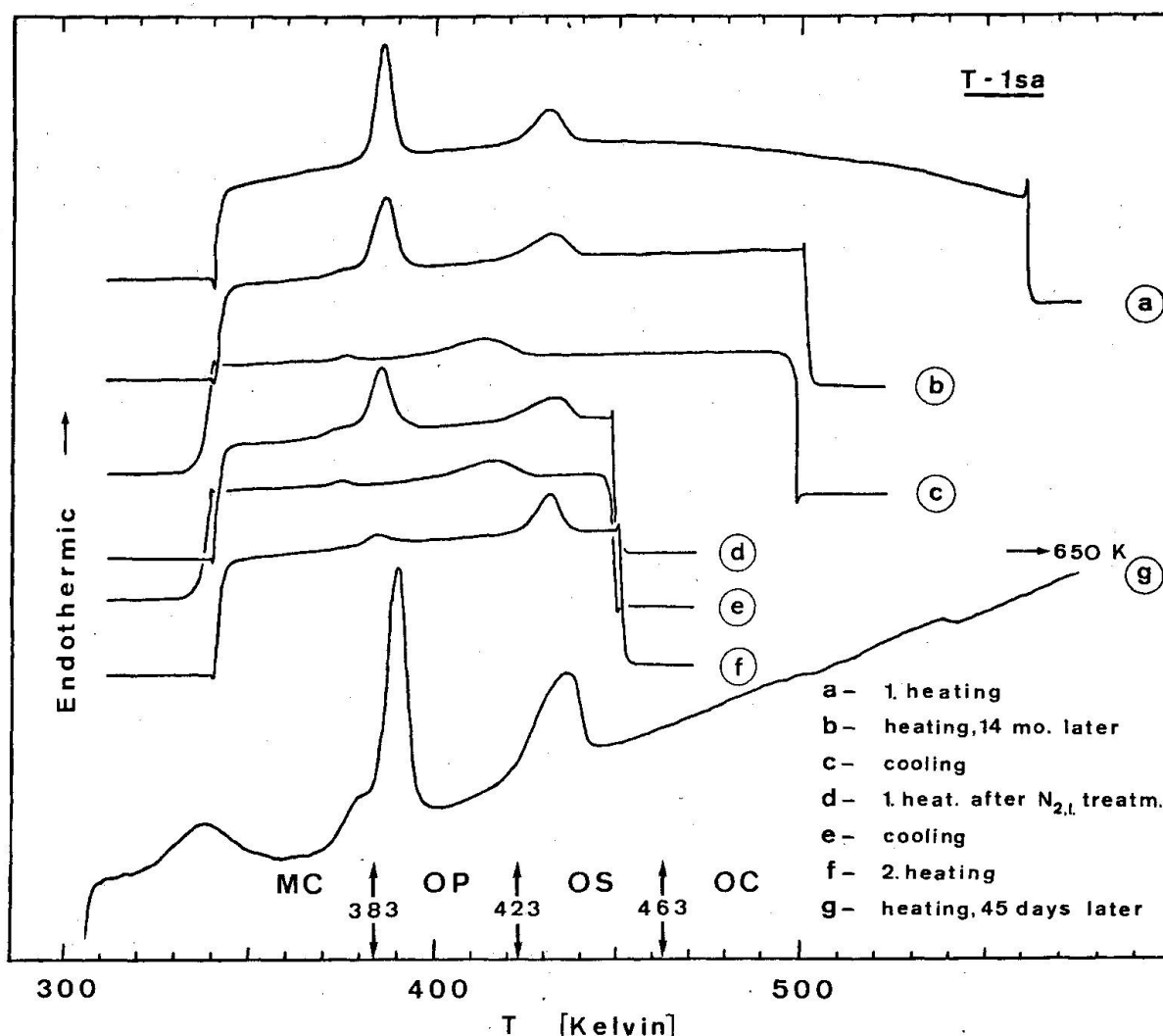
Figure 3 Tracings of DSC scans for T-1sa over narrow temperature ranges. Scan a ist the same as shown in Figure 1 a, b is a heating-scan made 14 months after scan a, and c is the immediate cooling-scan. Scan d is a heating-scan made after holding the sample in liquid nitrogen for one minute, scan e is the immediate cooling-scan and scan f represents an immediate second heating. The instrument settings were the same as given in Figure 1, except that the chart speed for scan b through f was 20 mm min^{-1}.

Scan g was made 45 days later on the same sample with the DSC-2C from 300 to 650 K. Here a shoulder to the 393 K peak was observed at 380 K and the 337 K peak is quite distinct.

trogen. The third peak in Li-TR near 521 K is interpreted as the transition of mechanically admixed crystals of cristobalite. This was verified by powder x-ray photographs which gave cristobalite reflections for Li- an K-TR (CARPENTER and WENNEMER, 1985). The difference in transition behaviour between structural-intergrowth and mechanical-mixture of tridymite and cristobalite crystals, may be seen by comparing Figure 1 and 2 with 4a. This has already been described by FLOERKE (1957, p. 346).

DSC-measurements on Na-TR made with greater DSC-sensitivity (Figure 4, c) revealed a peak near 515 K and this is interpreted as being due to cristobalite crystals in this sample too. The K-tridymite (Figure 4, d) showed a small peak at
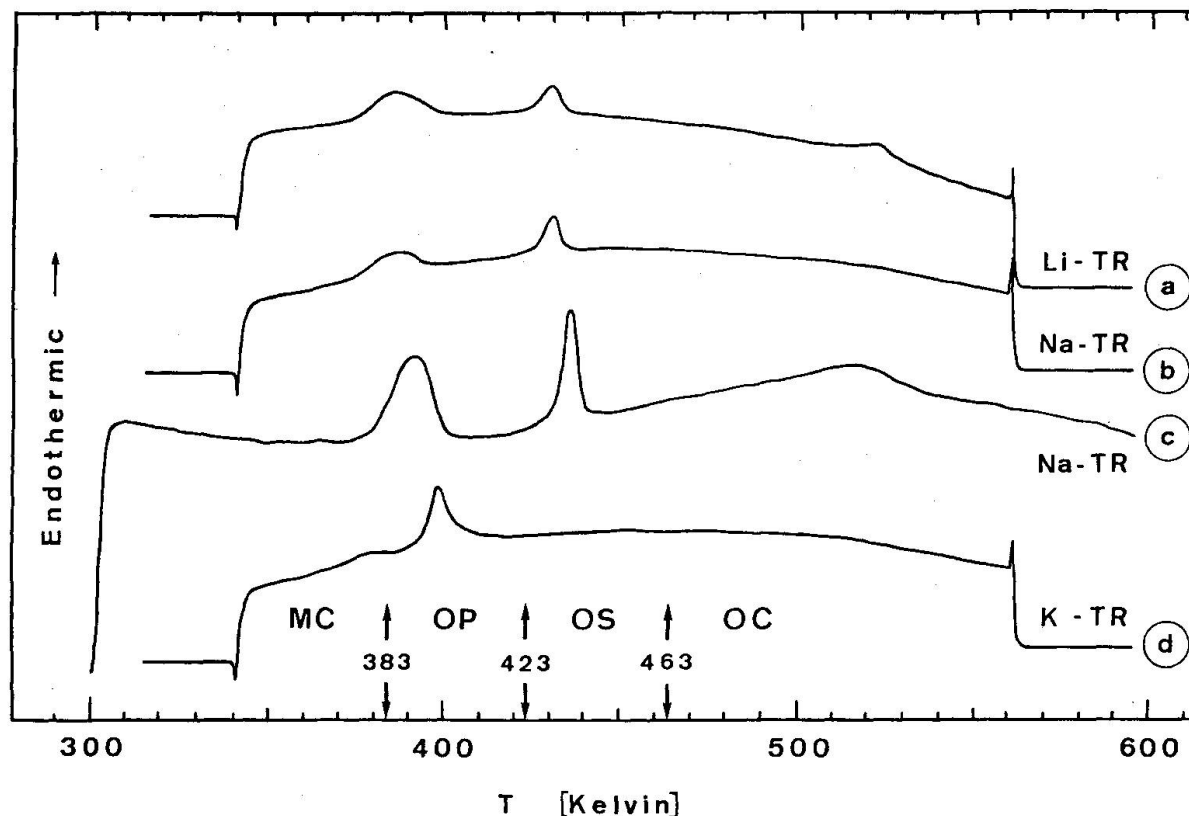
Figure 4 Tracings of the DSC scans for synthetic alkali-WO$_4$ fluxgrown tridymites over narrow temperature ranges. Scans a, b and d are first heating-scans from 340 to 560 K on the lithium, sodium and potassium fluxed preparations. Same instrument settings as in Figure 1 were used. The sample weights were about 24 mg for Li-TR and 30 mg for Na-TR and K-TR respectively. Scan c was made from 300 to 600 K on the DSC-2C, and revealed the 517 K peak in Na-TR.

378 K and a large transition at 398 K. According to FLOERKE and MÜLLER-VON-MOOS (1971, p. 200) the existence of only one transition is characteristic for strongly disordered tridymite. This interpretation was confirmed by the TEM-study of CARPENTER and WENNEMER (1985). The small peak at 378 K for K-TR (Figure 4, d) may be related to the shoulder on the 391 K peak of T-1sa (Figure 3, g). On the basis of what is known about tridymite and could be confirmed by the DSC-measurements, samples from various sources differ quite clearly concerning their transition behaviour. Not all the alkali-cations have the same efficiency in producing well ordered tridymite within an equivalent time, but it is the degree of structural order that determines the number and temperature of the transitions.

DSC RESULTS ON SOME NATURAL TRIDYMITES

The DSC heating results on some natural tridymites (from Plumas County and Mule Springs, Cat. No. 112499, provided by Dr. C. Francis, Harvard University) are shown in Figure 5. Other samples from Plumas County had previ-

ously been investigated by x-ray methods by Lukesh and Bürger (1942, p. 143), who found a single transition at 400 K using a controlled-temperature Weissenberg camera, and also by Konnert and Appleman (1978). The thermal behaviour of natural tridymites differs very much from that of the synthetic samples. The first heating of the Plumas County tridymite showed a broad peak which could be interpreted as a double peak with the two maxima near 405 K and 413 K and a shoulder at 427 K (Figure 5, a). On cooling, a single peak appeared at 370 K indicating a hysteresis of the transition of nearly 40 K (Figure 5, b). In the second heating-scan the shape of the broad peak had changed (Figure 5, c). The hysteresis could not be due to differing grain size as the same preparation technique was used for natural and synthetic samples. A single
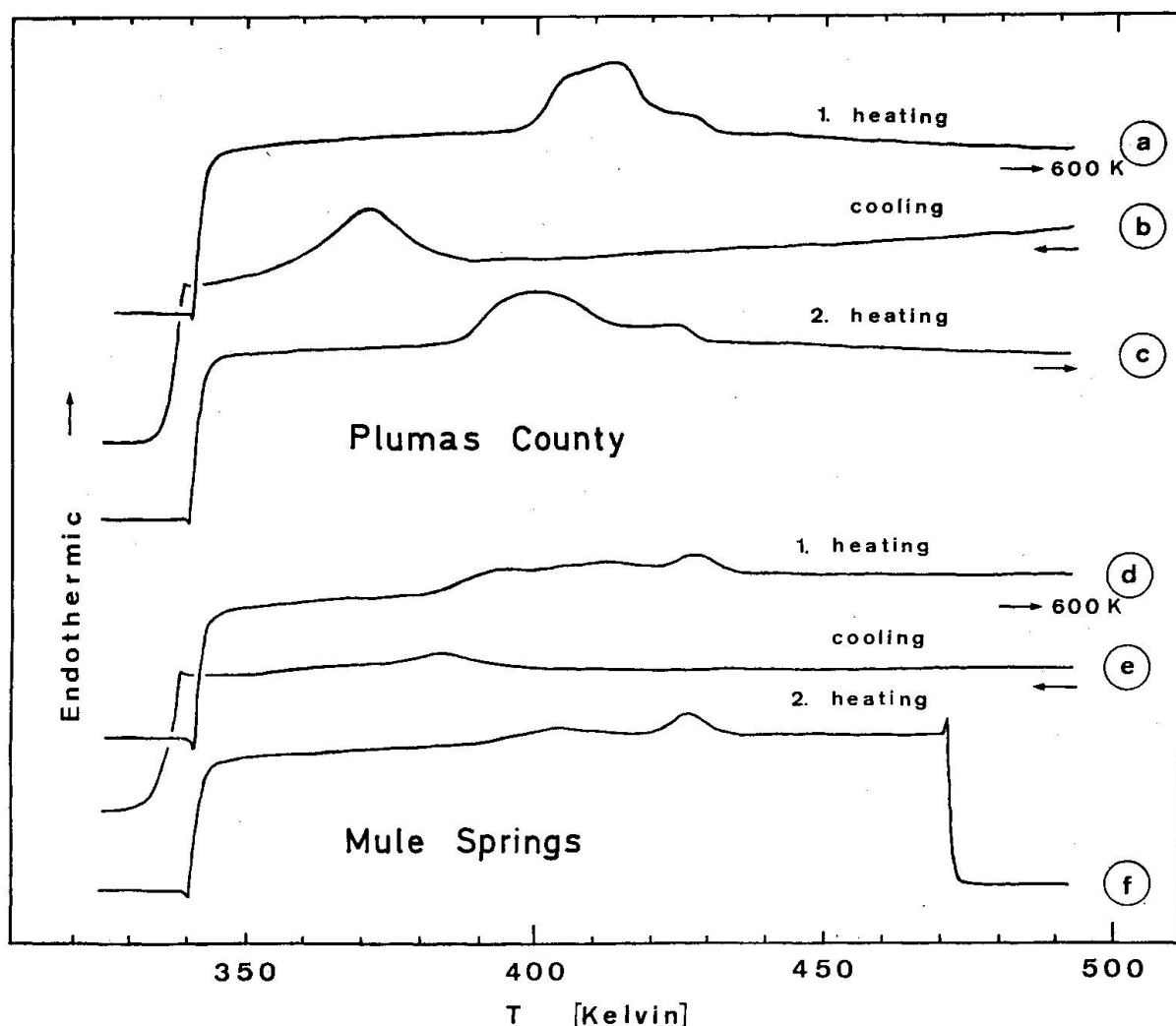

Figure 5 Tracings of the DSC scans for natural tridymite from 340 to 600 K a through e or 470 K, respectively. The instrument settings were the same as in Figure 1, except that the chart speed was 20 mm min⁻¹. The sample weight for each was about 30 mg. Scan a is a first heating-scan on the natural Plumas County tridymite, b the immediate cooling-scan. The hysteresis between the transitions in a and b is quite distinct. Scan c represents a second heating-scan. The same hysteresis in transition temperatures can be seen from the first heating-(d) and immediate cooling-(b) scans on the Mule Springs sample. The second heating-scan (f) differs quite clearly from d.

The two samples show little similarity with each other or with the synthetic tridymite samples.

maximum was observed at 398 K while the temperature of the shoulder re-mained nearly constant. Subsequent measurements supported these observa-tions. In contrast, LUKESH and BÜRGER (1942, p. 144) reported the transition to be irreversible and concluded that the sample must have formed below 394 K.

In the Mule Springs sample three effects could be observed (Figure 5, d), a very broad and flat double peak with maxima at 392 K and 410 K and a third larger peak near 428 K. On cooling only a single peak appeared near 384 K. The second heating-scan showed two single peaks, a broad-flat one at 403 K amalgamating the two previous peaks, and a sharper one at 425 K. Further DSC measurements gave the same results.

It is noteworthy that the 337 K transition observed in T-1sa, TR-III', Trid-G4 and TR-IV synthetic tridymites (Figure 2, a, b, c and d and Figure 3, g) was not observed in the scans for the alkali WO_4-fluxed tridymites and the two natu-ral samples. This was confirmed by measurements on the DSC in the range 300 to 630 K. Full details of the numerous DSC- and DTA-scans are given by WEN-NEMER (1983, Table 8).

LOW TEMPERATURE TRANSITIONS IN SYNTHETIC TRIDYMITE

Supporting the observation of a transition in synthetic tridymite at about 337 K, by HILL and ROY (1958, p. 506) and by SATO (1964, p. 219), the present DTA-measurements showed a small peak near 336 K for T-1sa and a larger peak for TR-III' (Figure 2). In TR-IV this small peak increased in intensity with increasing number of runs. A very weak effect could be detected in TR-G3 at 336 K but was absent in TR-800 and the pure cristobalite CR-1. According to these results the 337 K transition seems to be a real thermal effect. The small peak near 300 K is not considered to represent a tridymite transition, because it could also be observed in some blank (empty pan) runs as well as in cristobalite (Figure 2). All the samples, including the empty pan and the Al_2O_3-standard showed the water-freezing peak at about 281 K. Nevertheless, we need to be aware that any transition that occurs between 273–283 K would be overlapped by this "ice"-peak. No further transition could be detected at lower tempera-ture.

As SATO (1964) ascribes the 337 K transition to the transformation from S1 to S2, it was not clear why it could be observed in the T-1sa and the other sam-ples of the same type (TR-III', TR-G4 and TR-IV) as well. T-1sa, and conse-quently the other ones, definitely were of the MC-type (FLOERKE and cowork-ers, 1983). An explanation of this deviation from the expected transition behav-iour came from the observations made by HOFFMANN and coworkers (1983). They found that on grinding, MC-tridymite at least partially transforms to MX-1 tridymite. In the region 323 K to 368 K, MX-1 changes its structure to be-come a PO-10 type. On cooling not all of the PO-10 material transforms back to

MX-1 but is preserved down to room-temperature. A further possibility to produce MX-1 from MC is to quench original MC-crystals from above their MC-OP-transformation below room-temperature. For the interpretation of the DSC-results it is important that MX-1 crystals can transform back to MC, provided that parts of the crystals have preserved their MC-structure. The rate of this reverse transition increases at somewhat raised temperature.

CONCLUSIONS

On the basis of this new information the following explanation can be given for the transition behaviour. T-1sa, and at least the well ordered samples (Table 1), had the MC-structure. For the preparation for the DSC-measurements the material was ground, and by this, partially transformed to MX-1. Consequently at 330 K, the MX-1 to PO-10 transition could be observed (Figure 2, Figure 3 g) in those scans covering this temperature region. On the other hand, by starting the measurements (THOMPSON and WENNEMER, 1979, this work) at elevated temperature (360 K) and holding the sample at this temperature between subsequent runs, the reverse transformation of those MX-1 crystals formed by grinding, back to the original MC-structure was enhanced. As quenching should increase the amount of MX-1 in the sample, it is clear that (a) the 330 K transition in the DTA-measurements starting at 140 K could be detected easily, although those measurements did not start immediately after grinding and (b) the respective peak, for example in TR-IV, increased in intensity with increasing number of runs.

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