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THERMAL PROPERTIES OF TRIDYMITE: 25°C – 300°C

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Tridymite has been produced from a variety of fluxes. Most samples gave two first-order inversions at ~117 and ~163°. Calorimetric study shows that the heats of inversion exhibit considerable variation, and are thus not constants of tridymite. These differences are related to the polytypism and disorder. The 117° inversion occurs with considerable hysteresis: a method for determining equilibrium transition temperatures from dynamic data is presented. Some of the tridymite samples also exhibited a second-order inversion in the range 230—250°.

Preparation of tridymite

Quartz and silicic acid were used as starting materials. The quartz was supplied by Thermal Syndicate Ltd., and is crushed natural crystal selected for the manufacture of 'Specpure' silica glass. The silicic acid was supplied by Johns-Manville Co.: our analysis gave 84.70% SiO_2 the balance being almost entirely water, with only 0.02% material non-volatile with HF. The tridymite phase of silica cannot be formed directly from either of these starting materials. Fenner [1] found that sodium tungstate was an efficient flux for the interconversion of the low density silica modifications; tridymite formed in the range 870° – 1470°. Sodium tungstate was used in the present study: this and other fluxes were obtained as reagent-grade chemicals. The general procedure used in producing tridymite was to make a mechanical mixture of silica and an appropriate quantity of flux and to heat the mixture, contained in a platinum crucible, for the desired length of time in an electrically heated muffle. At the conclusion of a run the outside of the crucible was water-quenched to facilitate removing the sample. Conversion of quartz or cristobalite (the latter is formed rapidly from silicic acid) to tridymite was judged by petrographic examination and X-ray powder diffraction. The tridymitization is slow; runs of several hundred hours' duration may be required, even at 1300 – 1400°, to ensure complete conversion. The tungstate-fluxed samples were extracted by refluxing with 5% ammonium chloride solution, followed by two washings with 2% NaOH solution and finally with a double wash of 1% HCl solution and distilled water. This sequence of washings prevents precipitation of tungstosilicic acids and yields a very pure preparation of the appropriate silica phase. Microscopic examination showed that the extracted preparations contained laths or flat plates of tridymite, often growing as clusters or radiating wedges. The crystals were free of glass or flux inclusions. Only single-phase tridymite preparations were used for calorimetric work; for DTA and X-ray powder diffraction studies a wide range of other fluxes can be employed, but it is more difficult to ensure quantitative removal of any remaining glassy or crystalline phases.

The tridymite inversions

Inversion temperatures for tridymite have been reported based on a number of techniques; many observations have been based on DTA. In most cases, the inversion temperatures were obtained on the heating cycle only. Sinelnikov [2] studied both the heating and cooling cycles of tridymite and found that a tridymite which gave inversions upon heating at 114.5° and 162.5° gave the corresponding inversions at 72.4° and 148.1°, respectively, upon cooling. This immediately shows that a large hysteresis gap exists in the inversion temperatures found by DTA: in fact, Fenner's high-temperature optical studies on tridymite also suggest this possibility. It is not apparent from these studies which, if any, of these inversion temperatures represent the equilibrium* transformation temperatures.

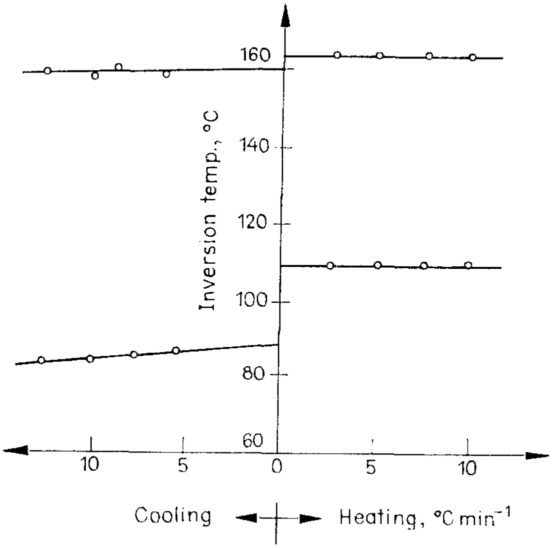

Fig. 1. Corrected inversion temperatures of a natural tridymite crystal at different heating and cooling rates

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* Strictly speaking, tridymite is metastable relative to quartz in the temperature range under consideration. Hence the 'equilibrium' is an apparent one.

An attempt was made to discover the equilibrium transformation temperatures, and to study the various factors which influence them. DTA patterns were obtained both on heating and cooling cycles for a range of programmed heating and cooling rates. These are summarized in Figs 1–4, which show the dependence of the observed inversion temperatures upon heating or cooling rate. The results include a small correction factor to allow for the changing response of the instrument at different heating and cooling rates. Using the macro-low temperature cell of a DuPont 900 DTA, this correction factor was never more than ±2–3° and is thus very small compared to the magnitude of the hysteresis which was observed in tridymite. The two separate portions of each recording – one representing heating, the other cooling – are not simply mirror images of each other. These rate data may be extrapolated back to a fictive zero heating rate to give an indication of the reversibility of the transformation. Both linear and logarithmic (log cooling rate vs. inversion temperature) extrapolations were tested; the data were found to fit a zero-order model over this range of heating and cooling rates. Fig. 1 shows data obtained from a natural single crystal. The inversions obtained upon heating occurred at essentially constant temperature over the range of heating rates from 2.5° $\min^{-1}$ to 10° $\min^{-1}$. Upon cooling, the inversions were quite sharp but were generally encountered at lower temperatures than on the heating cycle. For the high-medium inversion at ~160° the slope of the cooling rate–temperature plot indicates that, at zero cooling rate, the inversion would occur with little or no hysteresis. However, the middle-low inversion occurs with considerable hysteresis, which would apparently persist even at zero rate of temperature

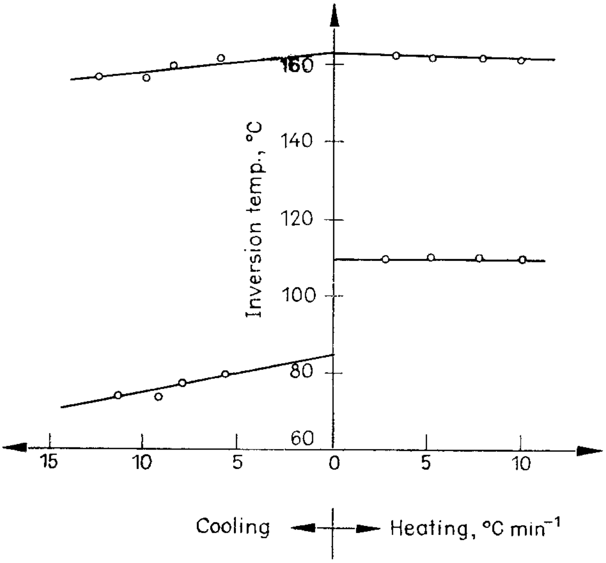

Fig. 2. Corrected inversion temperatures of tridymite grown from Na_2WO_4 flux at 1440°

change. The extent of the hysteresis is ~21° for this sample. Figs 2, 3 and 4 show the same type of data obtained for tridymites synthesised with sodium tungstate at temperatures of 1440°, 1325° and 1200°, respectively. In all cases, the high-middle inversions occur under conditions which are reversible, or very

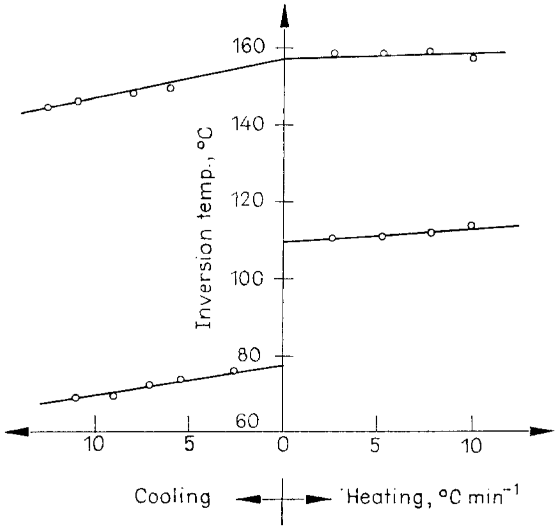

Fig. 3. Corrected inversion temperatures of tridymite grown from Na_2WO_4 flux at 1325°

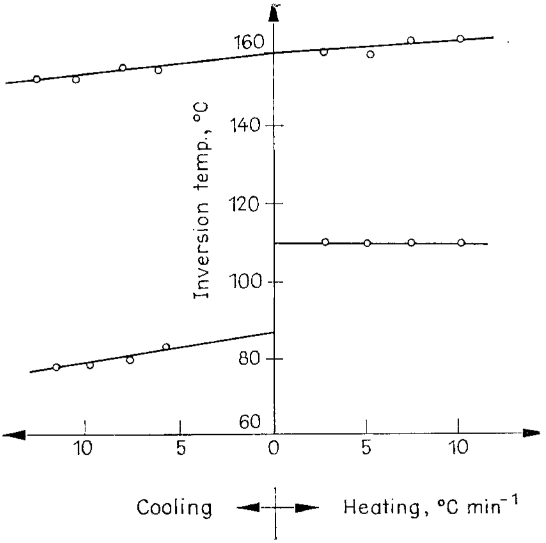

Fig. 4. Corrected inversion temperatures of tridymite grown from Na_2WO_4 flux at 1200°

nearly so, at zero rate of temperature change but a comparatively large hysteresis exists in the middle-low inversions. At zero rate the hysteresis ranges from ~25 – 35°. In all four samples the inversion temperatures determined on the cooling cycle show a more marked dependence upon cooling rate, as contrasted with the inversion temperatures determined at corresponding rates on the heating cycle.

As an additional test of the existence of this hysteresis gap, a sample of the tridymite, data for which are shown in Fig. 2, was used for the following experiment. The tridymite was heated at 8 – 10°/min to ~300°. At this point, the sample was cooled to 98° ± 2° at ~3°/min. The sample was held at this temperature for 30/min, and programmed cooling then begun at ~8°/min. The second inversion was encountered at 72°. Thus, holding the sample below the apparent equilibrium temperature for this time was not sufficient to cause inversion; it is considered that this evidence supports the existence of a real hysteresis gap.

Heats of inversion

Values for ΔH (transition) were measured for the low-middle and middle-high transitions using a DuPont dynamic calorimeter. The general design and theory of this calorimeter have been discussed by Boersma [3]. In the present study, the

Table 1

Low temperature phase transition in tridymites

Source of tridymite or literature reference			Inversion temperature, °C (heating)	ΔH cal mol^{-1}	Inversion temperature, °C (heating)	ΔH cal mol^{-1}
Mosesman and Pitzer [5]			163	40±10	117	70±10
Sabatier [10]			165	13.82	115	25.8
Sinelnikov [2]			162.5	35± 5	114.5	65± 5
Flux	Time (hrs.)	Temp., °C				
Li_2WO_4	72	1150	166*	31.0± 3	112*	69.0± 5
Na_2WO_4	48	1440	160	24.5± 2	114	79.0± 5
Na_2WO_4	356	1200	165	18.5± 2	112	72.0± 5
Na_2WO_4	672	1100	162	32.0± 3	113	83.0± 6
Na_2WO_4	504	1100	160	32.0± 3	113	76.0± 5
Na_2WO_4	96	1100	159	39.0± 3	115	70.0± 5
Na_2WO_4	75	1100	169	27.0± 3	114	82.0± 6
K_2WO_4	336	1250	160	10.0± 2	114	48.0± 5
			160	12.0± 2	114	40.0± 4
Natural tridymite †	—	—	165	24.0± 2	112.5	53.0± 5

* Temperatures below this point were determined by DTA, on the heating cycle, at 10° min^{-1} heating rate, and are accurate to ±2°. ΔH was determined in a seperate run made in the calorimeter cell.

† The tridymite was from a single subhedral crystal: locality unknown.

calorimeter was calibrated for specific heats using silica glass as a standard: values for C_p were taken from Morey's [4] compilation. Table 1 presents the values obtained from ten tridymite samples which were studied and compares these values with those in the literature. Owing to limitations of the apparatus, readings could only be obtained on the heating cycle. Values for ΔH are taken as the integral:

$$\int_{T_1}^{T_2} C_p \, dT$$

where C_p was the 'excess' heat capacity due to the inversion. The inversion appeared to spread over a definite interval of temperatures which was slightly wider than that which would be expected from instrumental effects only. The integration was done graphically. The values obtained show that the inversion temperatures remained nearly constant, but that ΔH values varied considerably from one sample to another. In particular, ΔH values for the middle-high inversion are generally lower than those found by Mosesman and Pitzer [5]. The variations in individual preparations made using Na_2WO_4 flux do not show any obvious correlation between either inversion temperatures or $\Delta H_{\text{transition}}$ and the time and temperature of preparation. Substitution of Li_2WO_4 for Na_2WO_4 does extend slightly the temperature range of existence of middle tridymite. The natural tridymite crystal gave rather low ΔH values for both inversions, rather resembling those tridymites which were produced from K_2WO_4 flux in this respect.

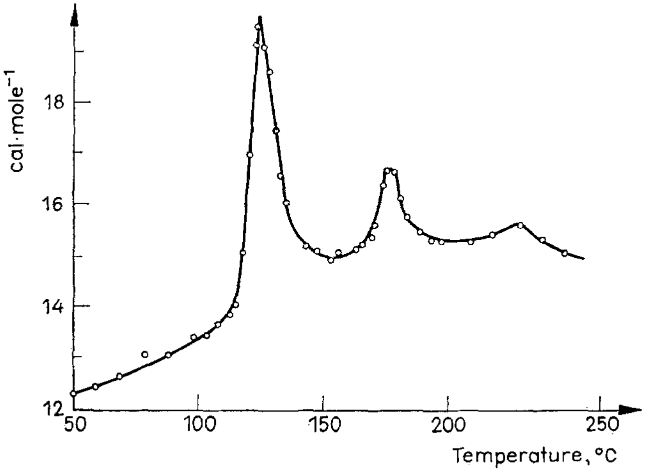

Fig. 5. Dynamic calorimeter scan of the heat capacity of tridymite grown from Na_2WO_4 flux at 1325°

Details of the heat capacity curves are shown in Figs 5 and 6. Fig 5 was obtained from a tridymite which had a characteristically high heat of inversion and sharp inversions. The main heat capacity peaks at ~117 and ~163° have a small 'tail' of excess heat capacity on the high-temperature side which produces slightly asymmetric heat capacity maxima. In addition to these inversions which are primarily first-order in their thermodynamic character, the heat capacity curve has a broad swell in the temperature range of 220° – 250°. Mosesman and Pitzer [5] also found an anomaly in this temperature range and interpreted it as indicating a first-order transformation at 225°. Fig. 6 shows the C_p data obtained from a K_2WO_4-fluxed tridymite. This is typical of the heat capacity spectra which were obtained from samples having comparatively small heats of transition. The effect at 220° – 250° is either missing or greatly reduced in magnitude. The C_p maxima in the vicinity of the ~117 and ~163° inversions are noticeably broadened and have a more pronounced second-order character, as compared with either the Na_2WO_4-fluxed samples or natural tridymite. Two scans are shown in Fig. 6. The sample was left in the calorimeter after the first run, cooled to below ambient, following which another scan was run. The two sets of data show the high degree of relative reproducibility which was obtained using the dynamic calorimeter: both curves show the same features. However, the absolute accuracy of the calorimeter is not high as compared with classical calorimetry; experience with replicate determinations shows that the absolute accuracy is approximately ±6 – 8% in scans which extend over a 200° temperature interval.

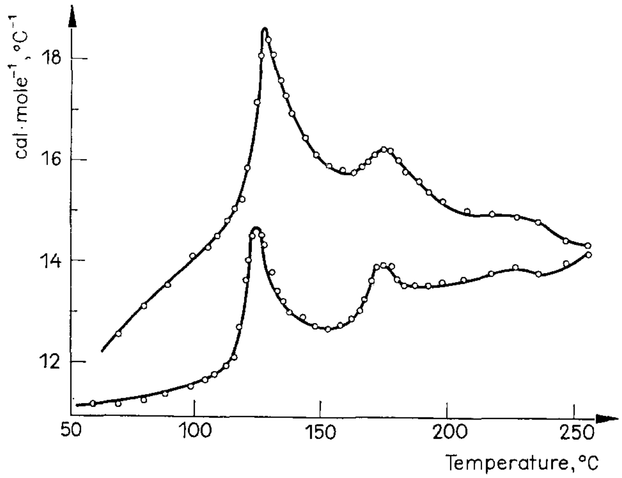

Fig. 6. Dynamic calorimeter scan of the heat capacity of tridymite grown from K_2WO_4 flux at 1325°

Internal structure of the tridymites

Two samples of tridymite which were studied gave crystals which were large enough for single-crystal X-ray photographs. The natural tridymite, examined at room temperature by rotation and Weissenberg methods, had an orthorhombic cell with $a = 5.01$ Å, $b = 25.7$ Å, $c = 48.6$ Å. The crystal was comparatively well ordered: most reflections gave sharp diffraction maxima, with only a little diffuse streaking around the very strong reflections. Crystals grown from a K_2WO_4 flux (336 hrs at 1250°) and examined at room temperature were also orthorhombic with $a = 4.97$ Å, $b = 51.3$ Å, $c = 97.8$ Å. Thus, the b and c axes of the latter were doubled relative to those of the natural tridymite. In addition, the K_2WO_4-fluxed tridymite was strongly disordered in the b and c directions. Powder X-ray diffraction data of this and the other tridymites in the range $20°-24°$ $2\,\Theta$ (Cu radiation) was obtained: according to Hill and Roy [6], the appearance of this position of the powder patterns can be used as a criterion of the relative crystallographic disorder of the tridymite. Sato [7] has criticised this scheme as being inadequate to represent the complex order–disorder phenomena which are known to occur in tridymites. From examination of these powder patterns and their comparison with single crystal photographs, as well as from powder X-ray data obtained from over 100 other samples, we agree with Sato's conclusions. Furthermore, optical evidence indicates the possibility that not all crystals in a given tridymite preparation need be exactly alike. The crystal selected from the tungstate-fluxed preparation was a lath which had sharp parallel extinction. Other crystals in the same preparation had undulose extinction; some appeared to have a small extinction angle.

Discussion

A number of inversions have been reported in tridymite: Sosman [8] distinguishes six polymorphic forms of well-ordered tridymite and three of less well ordered tridymite. It is impossible to prove that a given inversion which was reported in the literature was absent, but evidence for the two reported inversions at 64° and at 475° is very scanty. In the present study, at least one well ordered and one rather disordered crystal have been studied: both have very similar inversion schemes. Fig. 7 summarizes the probable polymorphic relations obtained in these tridymites at low temperatures and suggests a preferred nomenclature for the phases. The diagram shows a first order inversion between low and middle and between middle and high tridymite, and a second order inversion between high' and high tridymite. Arrows indicate the approximate reversibility of the paths; commonly encountered prolongations of phases are shown by single arrows lying on dashed extensions of the appropriate curves. The inversion temperatures shown are not constants; both solid solution and order–disorder relations cause appreciable variation. These possibilities are represented by a thickening of the lines as an indication that a slight variation in the free energy of an individual phase is possible even at a fixed temperature. It is also possible that other unusual tridymites may exist which exhibit different inversion schemes. However, addition of an excess of each of the following oxides: FeO, CaO, Al_2O_3 and GeO_2 at the $2-10\%$ level to the tungstate flux has produced only tridymites whose patterns of thermal activity conform closely to the scheme shown in Fig. 7. Although the tridymites studied have been grown from a number of different flux compositions at temperatures of 900–1450°, all have been found to have similar inversion scheme. Depending on the environment and history of the tridymite, the relative thermodynamic order of each of the transformations may be variable; the 230–250° transformation has been shown in Fig. 7 as a second-order transformation. Experimentally, this transformation is marked by a rather broad maximum in the heat capacity function. In theory this transformation could be detected by DTA but in practice it is less likely to be detected both because of the relatively small amount of energy change involved and also because of the "smeared" nature of the transformation. It must be recognized that the present data are rather at variance with those of Mosesman and Pitzer, who also found a phase change at 225°, but described it as a "sharp, rapid" transformation. They give ΔH transformation as 45 ± 10 cal mole^{-1}; it is difficult to integrate accurately the data obtained in the present study, however, a reasonable value for the 'excess' heat capacity in this range would be 10–20 cal mole^{-1}. The thermodynamic order of this inversion and also the size of the heat effect may be very variable for this inversion. One possible reason for the variable nature of this inversion is that it is due to the presence of cristobalite-like units incorporated in the tridymite structure. These "cubic" units undergo an $\alpha-\beta$ transformation which is smeared out, owing to the small size of the cristobalite units in the direction normal to the planes of closest oxygen packing. If this suggestion is correct, the character of this inversion or indeed, its absence, could be used as a guide to the relative amount of cristobalite-like units in a given tridymite.

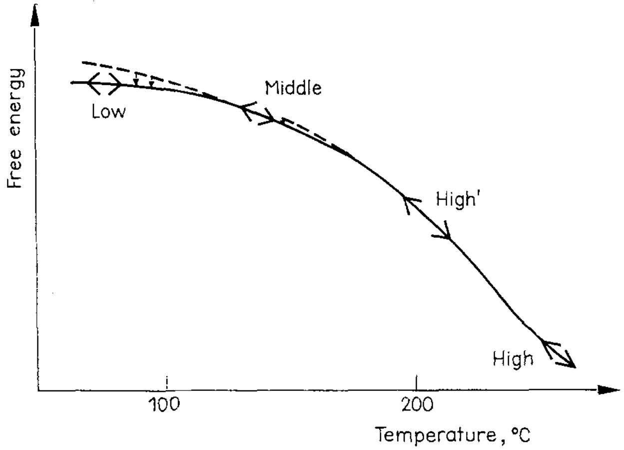

Fig. 7. Suggested free-energy vs. temperature relationships and nomenclature for the tridymites shown in Figs 5 and 6

Garn [9] has called attention to the widespread existence of supercooling and the occasional occurrence of superheating in inversions of the types solid$_1 \rightleftarrows$ solid$_2$. He was concerned with establishing the suitability of substances as standards for DTA calibration; therefore, in all cases the actual equilibrium transformation temperature of each particular inversion was known to a relatively high order of accuracy. A more general case arises where it is desired to establish accurately an equilibrium transformation temperature for an 'unknown' substance, using a dynamic technique such as DTA. While it might be possible to apply some of the criteria which were found by Garn as indicative of undercooling or superheating (for example, peak shapes), it is considered that the method of extrapolation to zero heating rate, as described in this study, offers a better method of estimating the true equilibrium transformation temperature of this type of inversions by dynamic methods. It is only necessary to extend the range of heating and cooling rates across a sufficiently wide range to estimate the kinetic order of the transformation in order that the correct extrapolation can be made.

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Résumé — On a préparé tridymite à partir de divers flux. La plupart des échantillons a montre deux inversions du premier ordre à 117 et 163°. Les chaleurs d'inversion montrent d'après l'étude calorimétrique des variations considérables et ne représentent pas des constantes de la tridymite. Les différences sont en corrélation avec le polytipisme et le désordre. L'inversion de 117° se produit avec un hystérésis considérable. On présente une méthode à déterminer les valeurs des températures de transition d'équilibre des données dynamiques. Plusieurs échantillons ont montré une inversion du second ordre à 230—250°.

Zusammenfassung — Es wurde über die Erzeugung von Tridymit aus verschiedenen Schmelzen berichtet. Die meisten Proben zeigten zwei Umwandlungen von erster Ordnung bei 117 und 163°. Kalorimetrische Untersuchungen zeigten, daß die Umwandlungswärmen beträchtliche Verschiedenheiten aufwiesen und keine Konstanten des Tridymits sind. Die Unterschiede sind auf Polytypen und Unordnungen zurückzuführen. Die Umwandlung bei 117° ist durch beträchtliche Hysterese begleitet. Es wurde eine Methode zur Bestimmung der Gleichgewicht-Übergangstemperaturen aus dynamischen Daten beschrieben. Manche Proben zeigten noch eine Umwandlung von zweiter Ordnung zwischen 230 und 250°.

Резюме — Тридимит был получен из разных расплавов. Наибольшее количество образцов обнаружило два превращения первого порядка при температурах — 117° и — 163°. Калориметрическое изучение показало, что теплоты превращения значительно меняются и не являются константами тридимита. Это указывает на политипизм. Превращение, наблюдаемое при температуре 117°, происходит со значительным гистерезисом; описан метод для определения равновесной температуры перехода по динамическим данным. Некоторые из образцов тридимита показали также превращение второго порядка в области температур 230—250°.