Crystalline transformation of Ti–B–O, Al–Ti–B–O, Si–Ti–B–O and Al–Si–Ti–B–O by thermal treatments

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The thermal transformations of Ti–B–O, Al–Ti–B–O, Si–Ti–B–O and Al–Si–Ti–B–O have been investigated using the methods of thermal analysis and X-ray powder diffraction. The materials are a crystalline series of TiO_2 with partial replacement of titanium by the elements, aluminium, boron and silicon. The anatase form of the materials was transformed to the rutile form at $520 \sim 680\,^\circ C$ for Ti–B–O, $880 \sim 950\,^\circ C$ for Al–Ti–B–O, $1080 \sim 1280\,^\circ C$ for Si–Ti–B–O and $1180 \sim 1330\,^\circ C$ for Al–Si–Ti–B–O. The rate constant for the anatase–rutile transformation of Ti–B–O was $6.908 \times 10^{-3}\ min^{-1}$ under isothermal conditions at $680\,^\circ C$. Analysis of the kinetic data obtained by differential thermal analysis (DTA) gave the activation energy for transformation of anatase into rutile as $663.7\ Kcal\ mol^{-1}$ for Al–Ti–B–O. The lattice parameters for the compounds studied at various temperatures were calculated by least-squares fitting of the X-ray powder diffraction data.

1. Introduction
In a previous paper [1], borosilicate Bolite-7 was reported to be an efficient catalyst for the cracking of n-icosane. The Bolite samples can be synthesized by a reaction of the various alkoxides with orthoboric acid using pyridine as a solvent. A family of Bolites includes, for example, Bolite-1 (Al–Si–Ti–B–O), Bolite-2 (Al–Ti–B–O), Bolite-3 (Al–Si–B–O), Bolite-4 (Si–Ti–B–O), Bolite-5 (Ti–B–O), Bolite-6 (Al–B–O), Bolite-A (Zr–B–O), Bolite-B (Zr–Al–B–O) and Bolite-C (Zr–Si–B–O).

In the present study, the thermal behaviour of Bolite-1, 2, 4 and 5 was investigated by means of thermal analysis and X-ray powder diffraction measurements. These Bolites can be obtained as isomorphous forms of TiO_2.

Titanium dioxide can exist in trimorphous forms: anatase, brookite, and rutile. Brookite is a naturally occurring phase with an orthorhombic system; it is extremely difficult to synthesize. Anatase and rutile with tetragonal crystallization, while occurring naturally, can be synthesized in the laboratory without difficulty; and it is well established that the anatase phase is irreversibly transformed to the rutile phase by thermal treatment. The anatase–rutile transformation is classified as a case of intermediate topotaxy [2, 3].

Recently, the transformation of TiO_2 has been investigated by R. I. Bickley *et al.* [4], who showed that thermal treatment of TiO_2 results in an amorphous phase. Such a study might elucidate the mechanism of the process and the presence of different phases under certain conditions.

This paper deals with the thermal treatment of Bolites containing titanium as a constituent in order to determine the presence of a different phase and to explain the mechanism of the transformation of anatase to rutile.

2. Experimental procedure
The preparations of Bolite-1, 2, 4, and 5 were the same as those used in an earlier study [5]. Various Bolite samples were heated to $1350 \pm 1\,^\circ C$ in a high-temperature furnace made by Advantec Toyo; the differential thermal analyses were carried out in air using a Rigaku Thermoflex TAS-200 at a linear heating rate of $10\,^\circ C\ min^{-1}$ with 20 mg samples in a platinum container.

X-ray diffraction (XRD) data were collected on a horizontal-type powder diffractometer with a Rigaku Geigerflex. CuK_α radiation at 40 kV and 30 mA, a nickel filter and a graphite monochrometer were used in all measurements. The scan speed used was usually $0.5 \sim 2.0^\circ\ min^{-1}$. A divergence slit of 1° and a receiving slit of 0.15 mm were used.

For the XRD measurements at high temperatures, the specimens were kept at a constant temperature for 5 h and cooled rapidly to room temperature. The diffraction lines could be indexed by a microcomputer (RINT). Silicon was used as an external standard and the correction values were subtracted from the experimental values. Accurate analysis of the data obtained was achieved by least-squares fitting of the standard powder pattern to the powder diffraction data obtained.
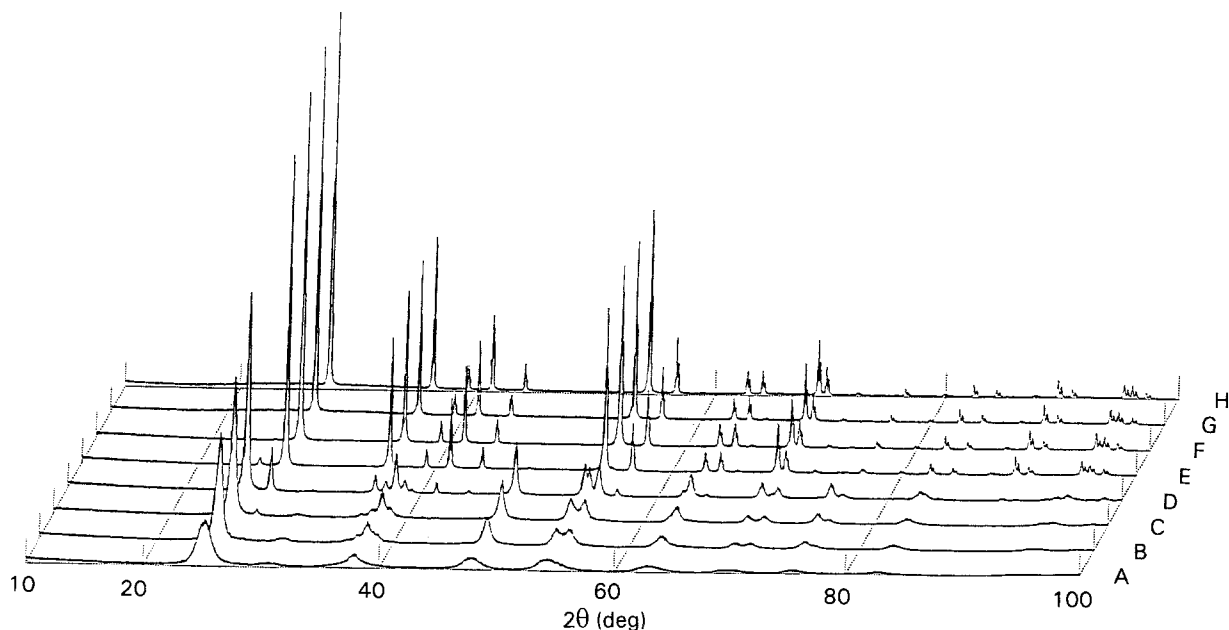
Figure 1 XRD patterns of the Bolite-5 sample for the following thermal treatments for 5 h: A, 60 °C; B, 480 °C; C, 520 °C; D, 580 °C; E, 680 °C; F, 780 °C; G, 880 °C; and H, 980 °C.

TABLE I The interplanar spacing d_{hkl} of the plane $(h\ k\ l)$ for the tetragonal Bolite-5 sample at 580 °C

Anatase	Rutile	Spacings, d(nm)	I/I_0
1 0 1		0.352009	100
	1 1 0	0.325003	23
	1 0 1	0.248867	10
1 0 3		0.242884	6
0 0 4		0.237802	20
1 1 2		0.233171	8
	2 0 0	0.229625	3
	1 1 1	0.218624	5
	2 1 0	0.205358	2
2 0 0		0.189232	26
1 0 5		0.169902	17
	2 1 1	0.168802	15
2 1 1		0.166428	16
	2 2 0	0.162371	5
2 1 5		0.149385	4
	0 0 2	0.147929	13
	3 1 0	0.145237	2
	3 0 1	0.135994	7
2 2 0		0.133695	6
2 1 5		0.126331	7
3 0 1		0.125031	3
	3 2 1	0.116478	5
	2 2 2	0.109297	2
	3 3 0	0.108275	1
3 0 5		0.105067	2
	4 1 1	0.104243	3
1 0 0		0.101724	2

Relative intensities were calculated from the relation $100\ I/I_0$, where I_0 is the intensity of the strongest line and I is the intensity of each peak height measured.

3. Results and discussion

3.1. Thermal behaviour of Bolite-5

The change in the XRD profile with temperature is shown in Fig. 1 for Bolite-5. The observed XRD lines of one crystalline system gradually disappear as treatment temperatures increase, while the line strengths resulting from the other crystalline system become more intense. The XRD patterns at lower temperatures were broader than those of the sample heated to various high temperatures as shown in Fig. 1. This broadening is due to the presence of water bound in the sample. The author suggests that the absence of a broad low baseline in the diffraction patterns at elevated temperatures is due to the high crystallinity of the sample.

On heating, X-ray diffractograms of the Bolite-5 (Fig. 1) show that the line at $2\theta = 27.46°$ first appears at 520 °C and the line at $2\theta = 25.296°$ disappears at 780 °C. X-ray lines indexable for the anatase and rutile forms at 580 °C are shown in Table I.

Two phases of Bolite-5 can be identified from their powder X-ray diffraction patterns, especially from the presence of the interplanar spacings of 0.35200 nm (1 0 1) for the anatase phase and 0.32500 nm (1 1 0) for the rutile.

The isothermal changes at 680 °C in the two kinds of spacings, i.e. (1 0 1) and (1 1 0), were determined for a sample of Bolite-5 previously heated to 480 °C for 5 h. For the semi-quantitative diffractometric measurements, the calibration graph was prepared using the anatase form of Bolite-5 after heating at 480 °C for 5 h and the rutile form resulting from Bolite-5 after heating at 780 °C for 5 h. From the plot of the integral strength of the peak area against the concentration, C, of a physical mixture of the samples of Bolite-5, straight lines of slopes with $314.4C^{-1}$ have been obtained for the anatase form and $864.2C^{-1}$ for the rutile form, respectively.

During the isothermal changes at 680 °C, the percentage compositions of both forms of anatase and rutile in the mixture are shown in Fig. 2 as a function of time. The curves show that the transformation of the anatase phase to the rutile phase proceeded rapidly in the initial stages and was complete in about 5 h.

The transformation of anatase to rutile of Bolite-5 by heat treatment is considered to be an irreversible first-order reaction. The value of the rate constant for
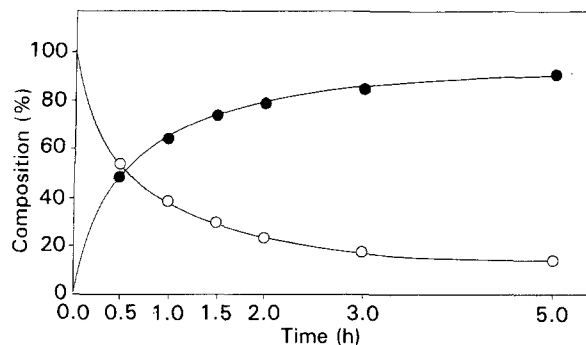
Figure 2 Isothermal curves for the thermal transformation of the Bolite-5 sample at 680 °C: (O) anatase, and (●) rutile.

Figure 3 Thermogravimetry (TG), DTA and integrated strength (IDTA) curves for the Bolite-2 sample.

the transformation of anatase to rutile for Bolite-5 is 6.908×10^{-3} min^{-1} at 680 °C, as determined from the data in Fig. 2.

In the experiments of the differential thermal analysis (DTA) of the samples of Bolite-5 preheated at 480 °C for 5 h, both exothermic and endothermic peaks in the temperature range from room temperature to 1000 °C were found to be absent. The same analyses of the anatase form of TiO_2 purchased from Kanto Chemical Company Inc., also showed no exothermic or endothermic effects on the DTA curves.

The Bolite-5 crystal is a tetragonal system with cell dimensions: $a = 0.378497$ nm, and $c = 0.949196$ nm for anatase at 480 °C; and $a = 0.458728$ nm, $c = 0.295748$ nm for rutile at 780 °C as determined from indexing its diffraction lines. The small changes in lattice parameters are recognizable by comparison with standard data for TiO_2 from the Joint Committee on Powder Diffraction Standards (JCPDS) cards Nos 21–1272 and 21–1276.

Figure 4 Determination of reaction kinetics for the Bolite-2 sample based on the IDTA value.

3.2. The thermal behaviour of Bolite-2

DTA of the compound of Bolite-2 preheated at 580 °C for 5 h gave an apparent exothermic peak in the thermal range 881.6–925.0 °C, with a maximum at 894.1 °C, as shown in Fig. 3. Careful repetition of the DTA experiments showed marked reproducibility, confirming the real occurrence of the exothermic peak in the curve which was not accompanied by any weight loss.

The kinetic method for the determination of reaction kinetics is based on a part of the DTA curve. The quantity of reacted substance is proportional to the area under the peak in the DTA curve. For the thermal transformation process of solid components belonging to the group of first-order reactions, the following expression given by Živković and Dobovišek [6] can be used.

$$\log \frac{\ln[S/(S - St)]}{t} = \log A - \frac{E}{2.303RT}$$

where E is the activation energy, A the frequency factor, R the universal gas constant, T the absolute temperature, S the area under the DTA peak up to the maximum reaction rate and St the area under the DTA peak after time t.
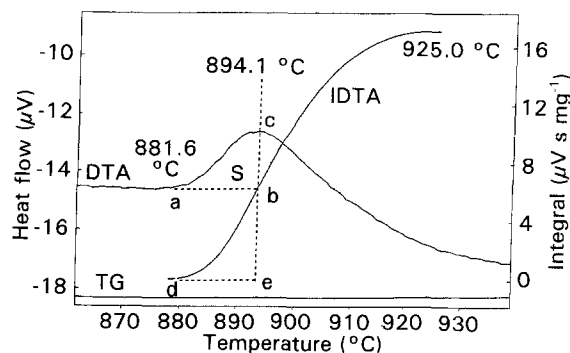
As for the observed process up to the maximum rate on the DTA curve, there are points a and c corresponding to points d and b on the curve of the integrated strength (IDTA) which was obtained with computed results from the DTA data. The value of S in the equation would represent the area of a, b and c, i.e. the height (b e) would represent the quantity S. The quantities St are denoted by the values at time t (sec) between d b on the IDTA curve.

In Fig. 4, a plot of $\log\{\ln[S/(S - St)]/t\}(s^{-1})$ versus the reciprocal of the absolute temperature $(10^3/T)$ shows that a linear relationship exists.

By the least-squares method, a slope of the most probable lines was determined, which made it possible to calculate the activation energy. The value of the activation energy for this case was found to be 663.7 Kcal mol^{-1}.

The changes in the XRD profile with temperature are shown in Fig. 5 for Bolite-2. The thermal transformation of anatase to rutile in Bolite-2 began at 880 °C and was complete at 980 °C. To obtain detailed information on the exothermic phase transition, XRD analyses were examined in detail over the temperature range from 780 to 980 °C. It is worth noting that the onset temperature of the transition of anatase to rutile
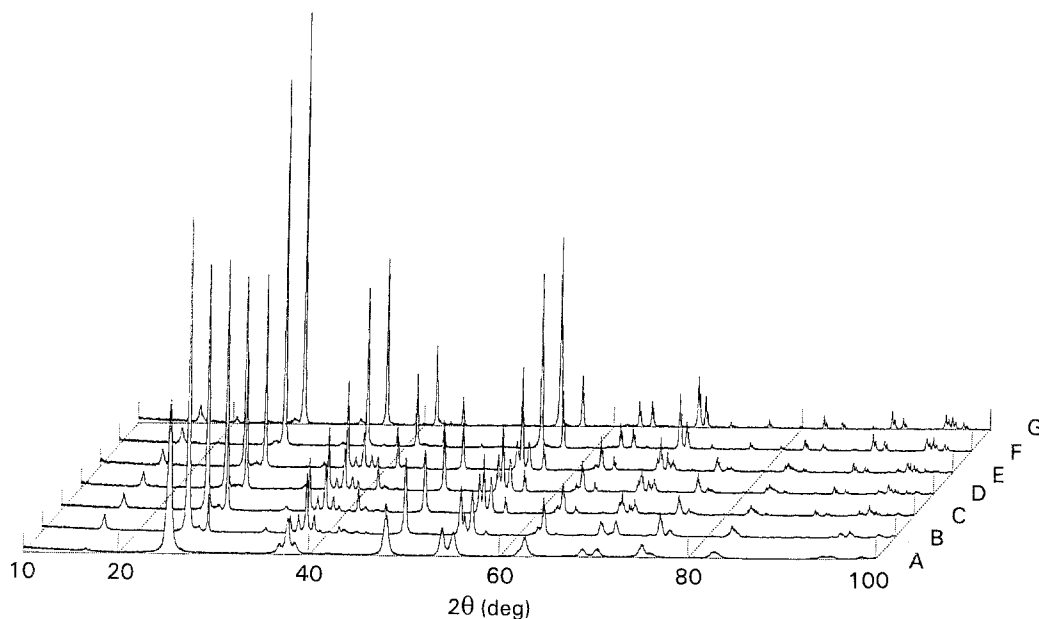
Figure 5 XRD patterns of the Bolite-2 sample for the following thermal treatments for 5 h: A, 780 °C; B, 880 °C; C, 881 °C; D, 894 °C; E, 925 °C; F, 950 °C; and G, 980 °C.
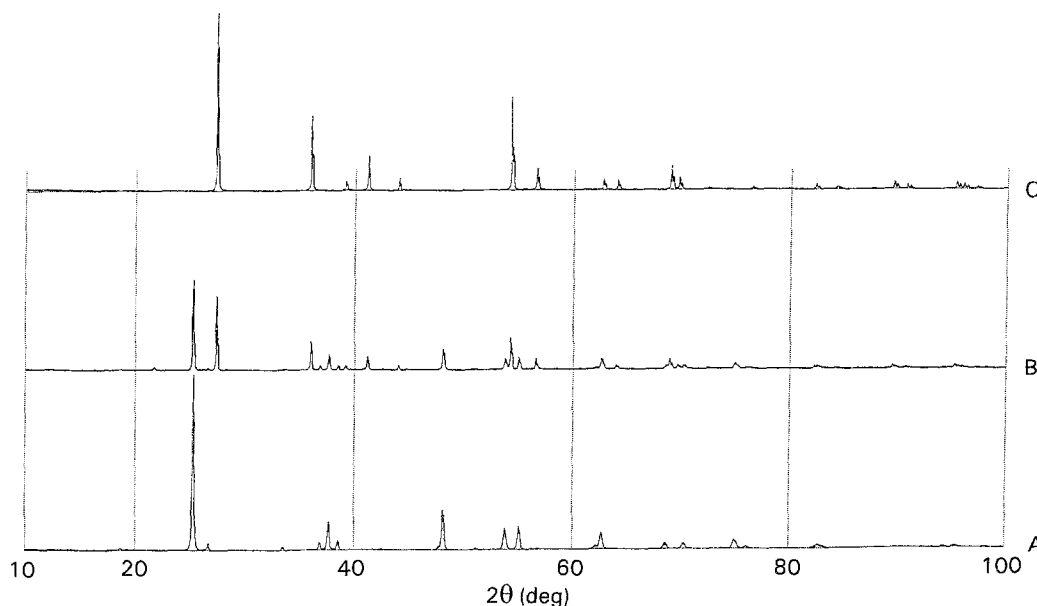

Figure 6 XRD patterns of the Bolite-4 sample for the following thermal treatments for 5 h: A, 1080 °C; B, 1180 °C; and C, 1280 °C.

at 880 °C is close to the temperature (881.6 °C) obtained from DTA experiments; whereas, the temperature giving rise to the complete rutile form, 980 °C, differs greatly from the DTA results. The result of the DTA experiment implies the reaction is complete at a temperature slightly over the maximum of the peak at 894.1 °C. Attempts to interpret these unusual results will be mentioned in a later section.

The Bolite-2 crystal is a tetragonal system with cell dimensions determined from indexing its diffraction lines: $a = 0.377873$ nm, $c = 0.949552$ nm for anatase at 800 °C; and $a = 0.458889$ nm, $c = 0.295726$ nm for rutile at 950 °C.

3.3. The thermal behaviour of Bolite-1 and Bolite-4

Above 1000 °C, there is a temperature limitation due to the thermal-analysis instrument. No changes were observed in the curves of the DTA up to 1000 °C for Bolite-1 and 4. The X-ray diffractograms of Bolite-1 and 4 in the temperature range 1080 to 1330 °C are shown in Figs 6 and 7. The anatase forms of Bolite-1 and 4 are stable at 1180 °C and 1080 °C, respectively, and then the transformation to the rutile form begins. The transformations end at 1330 °C for Bolite-1 and at 1280 °C for Bolite-4.

The compounds belonging to the tetragonal crystal system have the following lattice parameters: $a = 0.378401$ nm, $c = 0.951732$ nm for anatase at 1080 °C for Bolite-4; $a = 0.458734$ nm, $c = 0.295456$ nm for rutile at 1280 °C for Bolite-4; $a = 0.376556$ nm, $c = 1.037310$ nm for anatase at 1180 °C for Bolite-1; and $a = 0.459131$ nm, $c = 0.295705$ nm for rutile at 1330 °C for Bolite-1.
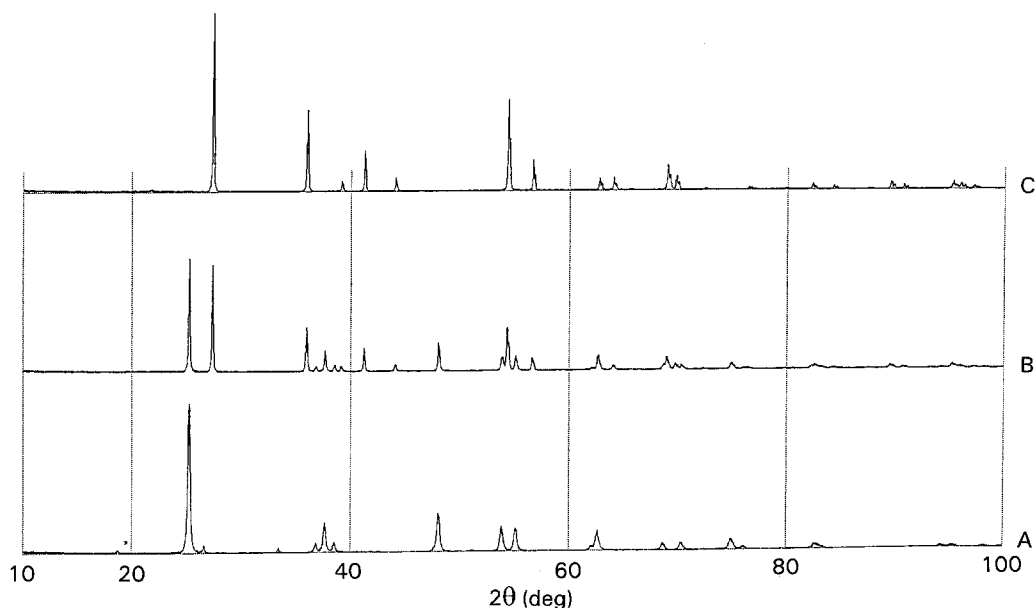
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Figure 7 XRD patterns of the Bolite-1 sample for the following thermal treatments for 5 h: A, 1180°C; B, 1280°C; and C, 1330°C.

3.4. Mechanism of thermal transformation

In these experiments, the critical temperature for the transformation of crystalline anatase to rutile is 520 °C for Bolite-5 crystals. A comparison of the information obtained by the XRD profiles and the changes in DTA studies leads to the presumption that a certain parallelism exists between the formation of the anatase–rutile transformation and the thermal effects.

During the thermal treatment, which produces the conversion from anatase to rutile, there must be a breakage of Ti–O or B–O bonds, producing a new linkage that will rearrange in the bulk lattice so that a transition to a more stable rutile phase occurs. However, no changes were observed in the DTA curve during thermal scanning of the sample up to 1000 °C. A comparison of the values of the standard enthalpy change of the formation of anatase of pure TiO_2 ($\Delta H = -224.6$ Kcal mol^{-1}) and rutile ($\Delta H = -225.8$ Kcal mol^{-1}) [7] suggests that a small difference in ΔH values of the two phases has a minor effect on the DTA curve. In this connection, it is worth recalling that a Bolite-5 compound has a small but noticeable range of boron amounts in the crystal [5]. It is probable that the presence of a small amount of boron incorporated within the crystal lattice has no effect on the ΔH value of TiO_2.

The co-ordination number of oxygen around Ti^{4+} for TiO_2 is six, and the packing structure of oxygen is the distorted cubic close packing (c.c.p.) for anatase and the distorted hexagonal close packing (h.c.p.) for rutile. During the phase transformation of anatase to rutile, two Ti–O bonds in a TiO_6 polyhedron must be broken. Then Ti^{4+} and O^{2-} move co-operatively; that is, Ti^{4+} moves from an octahedral site to a new octahedral site and the packing structure of oxygen changes from c.c.p. to h.c.p. [3]. A combination of hetero-atoms such as Ti and B will produce an irregular crystalline lattice or certain oxygen vacancies in the bulk lattice.

The crystal ionic radius of Ti^{4+} for sixfold co-ordination is 0.075 nm, which is larger than that of B^{3+}, 0.025 nm, for fourfold co-ordination. When the Bolite-5 sample was heated above 300 °C in H_2, the colour of the Bolite-5 sample changed from white to dark violet. On cooling, the colour was readily restored. The white colour of pure titanium dioxide did not change markedly under the same experimental conditions. The colour changes in the Bolite-5 sample seem to be related to the ready formation of oxygen vacancies through dehydration by hydrogen and reduction of the Ti^{4+} ion to Ti^{3+}. Therefore, the lattice unit of Bolite-5 may have voids which can accept a larger amount of other gases, and these voids can possibly lead to the formation of active sites which permit its use as a catalyst for various reactions and as a solid-state electrolyte [8].

The results obtained in the XRD study of the anatase–rutile transformation of Bolite-2 showed that the transformation started at 880 °C and was complete at 980 °C. If the exothermic effects are due to the simple anatase–rutile transformation, then it would be expected that the change in the X-ray pattern should be almost complete at a temperature slightly over the maximum of the peak in the DTA curve. The theoretical analysis of the DTA curve has been studied by Vold [9]. The activation energy for the anatase–rutile transformation is necessary to break the Ti–O and Al–O bonds as these atoms redistribute to reach their new configuration. The lack of close similarity between Al and Ti atoms suggests the necessity of energy differences in a rearrangement of these atoms in new crystal frameworks.

There are differences in the bond strength between Ti–O and Al–O; that is, the values of the bond energies for Ti–O and Al–O are 167 ± 2 and $127 \sim 138$ Kcal mol^{-1}, respectively [10]. Although the value of Al–O is lower than that of Ti–O, a large input of energy is necessary for the transformation of Bolite-2 compared

TABLE II Lattice parameters a, c (nm) for the Bolite-2 sample at various temperatures

		Temperature (°C)				
		800	880	894	925	950
Anatase	a(nm)	0.377873	0.378033	0.378117	0.378338	–
	c(nm)	0.949522	0.950696	0.951074	0.952143	–
Rutile	a(nm)	–	0.459241	0.458582	0.459057	0.458889
	c(nm)	–	0.295834	0.295765	0.295773	0.295726

to that for Bolite-5. The large requirements of energy in the transformation of Bolite-2 may be due to other factors. One possibility may be that the anatase form of Bolite-2 is composed of networks of more loosely linked polymers with higher potential energy than Bolite-5, and a distorted lattice is required to liberate energy.

The question must therefore be why the anatase phase still remains in the sample after the end of the exothermic reaction. If the exothermic effects are due to the simple anatase–rutile transformation, then it would be expected that the changes in the XRD pattern at 894.1 °C should be almost complete by this temperature. The disparallelism between the exothermic effect and the XRD change means that the phase transition cannot be a simple, single-stage transformation. One possibility, which would explain this apparent deviation, is the development of an intermediate mixed structure in the transition region. That is, the thermal effect produces an irregular distorted-lattice intermediate product or a tetragonal anatase-related structure which is necessary for the formation of a perfect crystal. Therefore, it is worthwhile examining the lattice parameters in the system showing the presence of both anatase and rutile in varying proportions by thermal treatments.

The lattice parameters of Bolite-2 at 800, 880, 894, 925 and 950 °C are given in Table II. In the first stage of the transformation at 880 °C, the lattice parameters show little change from those of the parent anatase at 800 °C. The changes in the lattice parameters of the anatase phase at 894 and 925 °C show the lengths of the a-axis and c-axis are larger than the data at 800 °C. However, the lattice parameters for the rutile phase at those temperatures remain substantially unchanged compared with the values obtained at the higher temperature ranges which cause conversion to the complete rutile form.

Hence an explanation for the transformation of the present well-crystallized Bolite-2 involves the hypothesis that the reaction occurs according to the following scheme.

Anatase → [quasi-anatase] → Rutile
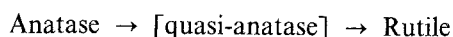
The activation energy becomes available in the initial stage of the transformation of the anatase phase to the transition state as a first-order reaction; that is, the anatase form begins to change to a quasi-anatase as an intermediate phase on heating from 881.6 to 894.1 °C with an exothermic reaction. It seems probable that the subsequent transition phase may be amorphous or may involve a catastrophic transition of quasi-anatase

into rutile. The present study does not include the precise measurements of enthalpy changes for the transitional product. It may be, however, that the reaction is the thermodynamically favoured route.

3.5. Thermostability of the crystals of Bolite-1 and 4

The compounds of Bolite-1, 2, 3 and 4 were shown to be isomorphous by the XRD patterns. They are a crystalline series of TiO_2 with partial replacement of titanium by the elements, aluminium, boron and silicon.

The structural unit of Bolite-1 and 4 is a tetrahedron in which each silicon atom is covalently bonded to four oxygen atoms, and the variation is in the ways these tetrahedra are interconnected by oxygen atoms to form a three-dimensional system. The large number of crosslinks per $[SiO_4]^{4-}$ unit leads to a material which is a stable inorganic polymer. Other factors which influence the properties of polymers can be explained by examining the bond energies or bond strengths and the ionic character of bonds based on Si as contrasted to similar bonds based on aluminium, boron or titanium. A silicon–oxygen linkage is stronger than any of the others, and this is reflected in the excellent stability of crystals of Bolite-1 and 4.

Titanium silicate (TS-1) is, according to Taramasso et al. [11], particularly useful for the following: (i) cracking and hydrocracking, (ii) reforming, (iii) methanol to gas (MTG) processes, (iv) degradation of hydrocarbons which contain olefinic or acetylenic bonds, and (v) oxidation.

The excellent thermostability of Bolite-1, 2 and 4 look particularly attractive for a wide spectrum of energy-conversion technologies and for industrial applications, including three-way catalysts, photocatalysts and advanced ceramics.

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