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Phase Relations in the Pseudobinary System TiO_2–Ga_2O_3

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Phase relations and microstructures in the TiO_2-rich part of the TiO_2–Ga_2O_3 pseudobinary system have been determined at temperatures between 1373 and 1623°K using X-ray diffraction and electron and optical microscopy. The phases occurring in the system are TiO_2 (rutile), β-Ga_2O_3, a series of oxides $Ga_4Ti_{m-4}O_{2m-2}$ (m odd) which exist above 1463°K, and Ga_2TiO_5, which exists above 1598°K. The width of the phase region occupied by the $Ga_4Ti_{m-4}O_{2m-2}$ phases varies with temperature. At 1473°K it is narrow, and has limits of $Ga_4Ti_{25}O_{56}$ to $Ga_4Ti_{21}O_{48}$ while at higher temperatures it broadens to limits of from $Ga_4Ti_{27}O_{60}$ to $Ga_4Ti_{11}O_{28}$ at 1623°K. These phases are often disordered and crystals frequently contain partially ordered intergrowths of oxides with various values of m. On the TiO_2-rich side of the phase region there is a continuous change in texture from rutile to the end members of the $Ga_4Ti_{m-4}O_{2m-2}$ structures. The findings are summarized on a phase diagram.

Introduction

The Ga_2O_3–TiO_2 system was first studied from a phase analytical viewpoint by Lejus *et al.* (*1*). These authors reported a ternary phase of apparently wide stoichiometry range which was stable above 1570°K but they did not report the structure of this material. The only other ternary phase found was the pseudobrookite Ga_2TiO_5.

Gibb and Anderson (*2*), in an electron microscope study of a number of M_2O_3–TiO_2 oxide systems which included the Ga_2O_3–TiO_2 system, discovered a series of oxide phases represented by the formula $Ga_4Ti_{m-4}O_{2m-2}$ with m able to take the odd values between 15 and 23 which they equated with the unknown phase of Lejus *et al.* Structurally these phases were composed of lamellae of rutile, joined along {210} planes. If the thickness of the rutile lamellae were uniform, an ordered member of the $Ga_4Ti_{m-4}O_{2m-2}$ series would be obtained, with the value of m depending upon the thickness of the rutile slab. The actual structure of the boundary region between adjacent slabs was not determined, and the nature of these {210} boundaries was left open to question.

In a recent paper, Bursill and Stone (*3*) confirmed the existence of these oxides and suggested a structure for the boundaries which has since been confirmed by Lloyd *et al.* (*4*) who determined the crystal structure of one of the oxides, $Ga_4Ti_{21}O_{48}$. The boundary regions can be thought of best as thin sheets of β-Ga_2O_3 coherently intergrown with the TiO_2 lamellae and linking them together. As the anion packing in the β-Ga_2O_3 boundary region is somewhat different than in the rutile lamellae on either side, these latter are displaced from one another by a vector $[-\frac{1}{2}\,\frac{1}{4}\,\frac{1}{2}]$ and the {210} boundaries can also be looked upon as crystallographic shear (*CS*) planes derived by the operation $[-\frac{1}{2}, \frac{1}{4}, \frac{1}{2}]$ (210) on the rutile structure. As a description in terms of intergrowth of β-Ga_2O_3 is chemically lucid we shall

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employ it in this paper, and refer to the $Ga_4Ti_{m-4}O_{2m-2}$ oxides as intergrowth phases rather than *CS* phases.

Although the results cited above have clarified the structural aspects of the TiO_2–Ga_2O_3 system, a number of other questions remain unanswered. In particular the composition and temperature range over which the intergrowth phases occur is not known in detail. In addition, Gibb and Anderson (*2*) indicated that TiO_2 was able to support at least a 2 mole% solid solution of Ga_2O_3 at 1570°K, although Lejus *et al.* (*1*) do not indicate any solid solution range for TiO_2 on their phase diagram. To clarify these uncertainties we have made a study of the phase relations in the TiO_2–Ga_2O_3 pseudobinary system up to 1623°K. This paper describes the results of this work.

Experimental

The chemicals used in this study were TiO_2 (grade 2) ex Johnson Matthey and Ga_2O_3 (3N) ex Koch–Light. Appropriate mixtures of these were weighed to give overall compositions of between 0 and 60 mole% Ga_2O_3, ground together in an agate mortar under methanol and pressed into pellets. The majority of these pellets were heated in air on platinum foil at temperatures of between 1373 and 1623°K for times varying from several days to 1 month. After reaction, the samples were quickly removed from the furnace to air but were not quenched in any other way. Some pellets were given similar treatment to those just described but were contained in sealed platinum ampoules while others were arc melted under an argon atmosphere before subsequent annealing under the same conditions as the air fired pellets. In addition a few samples were heated at temperatures higher than 1623°K and some preparations were made using single-crystal TiO_2. These latter experiments will be described fully in a future communication.

The phases present in reacted samples were determined by recording their X-ray powder photographs taken at room temperature with a Guinier–Hägg focusing camera using strictly monochromatic $CuK\alpha_1$ radiation and KCl ($a = 0.62923$ nm at 25°C) as an internal standard. Lattice parameters were refined using least-squares techniques (*5*). The microstructure of samples was studied using a Zeiss Ultraphot optical microscope and a JEM 100B electron microscope operated at 100 kV and fitted with a goniometer stage. Samples were prepared by crushing selected fragments of reacted material under n-butanol in an agate mortar; drops of the resultant suspension being allowed to dry upon netlike carbon support films (*6*). Only those crystals lying over holes in the support film were photographed.

Results

Initial preparations by arc melting were found to contain a fair amount of more or less well-ordered crystal flakes of the $Ga_4Ti_{m-4}O_{2m-2}$ intergrowth oxides. The X-ray diffraction patterns of these samples were, however, poor, and not suitable for phase analysis, but they did show that the disordered intergrowth oxides gave patterns which could be distinguished from the other phases expected to be present, TiO_2, β-Ga_2O_3, and $GaTi_2O_5$.

Using this information as a starting point, a series of solid state preparations were made. Although these resulted in sharper X-ray diagrams, there was some evidence to suggest that true equilibrium had not been achieved. In particular, samples which were rich in gallia often contained rutile and some intergrowth oxides as well as β-Ga_2O_3 or $GaTi_2O_5$ if the temperature was high enough. Longer heating times (of up to 1 month) and higher temperatures did not alter this, suggesting that failure to reach equilibrium was not simply due to kinetic factors, and alternative reasons were sought. As examination of the same specimens by optical microscopy suggested that there was a change in gross phase

TABLE I

LOSS OF WEIGHT OF TiO_2/Ga_2O_3 PELLETS AFTER HEATING IN AIR FOR 14 DAYS AT 1623°K

Starting comp. (Ga_2O_3 mole%)	Starting weight (g)	Weight after heating (g)	Weight loss (g)	Weight loss (wt%)	Composition after heating (Ga_2O_3 mole%)
5	1.93700	1.93626	0.00074	0.04	4.97
10	1.96739	1.96520	0.00219	0.11	9.95
15	1.93409	1.93120	0.00289	0.15	14.93
20	1.94689	1.94371	0.00318	0.16	19.93
50	1.96047	1.95687	0.00360	0.18	49.93

structure between the inside of pelleted samples and the surface layers, volatility of Ga_2O_3 was suspected to be responsible.

This was shown to be the case and was confirmed in two ways. First, a number of samples were heated at 1623°K in sealed platinum tubes instead of air. The X-ray photographs from these were compatable with an equilibrium situation. Second, a number of pellets were carefully weighed before and after heat-

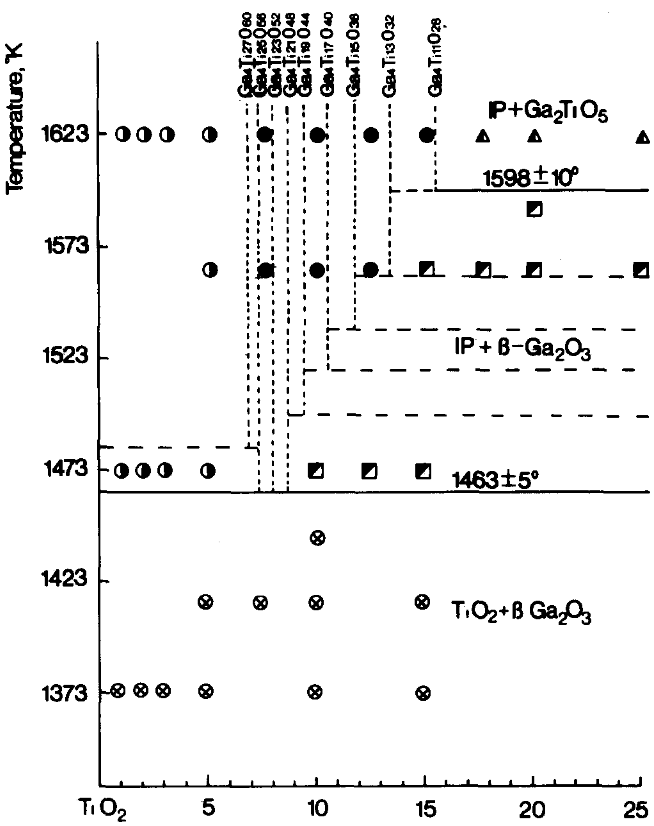

FIG. 1. Postulated equilibrium phase diagram of the pseudobinary system TiO_2–β-Ga_2O_3. Broken lines refer to suggested equilibrium phase boundaries which have not been definitely located in this study. ◑, TiO_2 (rutile) + disordered I.P.; ●, disordered I.P.; ▲, I.P. + Ga_2TiO_5; ◪, I.P. + β-Ga_2O_3; ⊗, TiO_2 (rutile) + β-Ga_2O_3; I.P., $Ga_4Ti_{m-4}O_{2m-2}$ intergrowth phase(s).

TABLE II

EXPERIMENTAL RESULTS FOR COMPOSITIONS IN THE PSEUDOBINARY TiO_2–Ga_2O_3 SYSTEM

Sample no.	Composition (mol% Ga_2O_3)	Heating temperature (°C)	Heating time (day)	X-ray diffraction phase analysis
147	1.0	1350	7	T + I.P.
146	1.0	1200	12	T + I.P.
143	1.0	1100	14	T + G
138	2.0	1350	7	T + I.P.
140	2.0	1200	8	T + I.P.
144	2.0	1100	14	T + G
139	3.0	1350	7	T + I.P.
141	3.0	1200	8	T + I.P.
145	3.0	1100	14	T + G
69*	5.0	1350	14	T + I.P.
80	5.0	1350	14	T + I.P.
11	5.0	1290	7	T + I.P.
59	5.0	1290	(7) + 18	T + I.P.
94	5.0	1200	14	T + I.P.
112	5.0	1140	12	T + G
106	5.0	1100	15	T + G
70	7.5	1350	14	I.P.
60	7.5	1290	28	I.P.
95	7.5	1200	14	I.P.
113	7.5	1140	12	T + G
71*	10.0	1350	14	I.P.
81	10.0	1350	14	I.P.
12	10.0	1290	7	I.P.
61	10.0	1290	(7) + 18	I.P.
96	10.0	1200	14	I.P. + G
135	10.0	1170	7	T + G
114	10.0	1140	12	T + G
107	10.0	1100	15	T + G
72	12.5	1350	14	I.P.
62	12.5	1290	28	I.P.
97	12.5	1200	14	I.P. + G
73*	15.0	1350	14	I.P.
82	15.0	1350	14	I.P.
13	15.0	1290	7	I.P.
63	15.0	1290	(7) + 18	I.P. + G
98	15.0	1200	14	I.P. + G
115	15.0	1140	12	T + G
108	15.0	1100	15	T + G
74	17.5	1350	14	I.P. + P.B.
64	17.5	1290	28	I.P. + G
75	20.0	1350	14	I.P. + P.B.
14	20.0	1290	7	I.P. + G
65	20.0	1290	(7) + 18	I.P. + G
51	25.0	1350	8	I.P. + P.B.
15	25.0	1290	7	I.P. + G
89	20.0	1320	6	I.P. + G

Note: T; rutile TiO_2. I.P.; intergrowth phase. P.B.; pseudo-brookite Ga_2TiO_5. G; gallia Ga_2O_3. *; heated in a sealed platinum tube.

ing at 1623°K in air. These results, shown in Table I, revealed that small but definite weight losses had occurred. Optical microscopy suggested that serious depletion of Ga_2O_3 was confined to a relatively thin surface layer. X-ray photographs of material taken from the surface of these pellets invariably showed the presence of rutile as well as any other phases present even in gallia-rich preparations while X-ray photographs of material from the center of the pellets were in agreement with the X-rays of samples heated in platinum tubes, and did not show rutile to be present in gallia-rich material.

These results showed that spurious conclusions could be drawn if only the surfaces of the pellets were examined subsequent to heat treatment. In order to obtain valid equilibrium data all later experiments used only the center portion of large pellets of starting materials. The results obtained in this way were self-consistent and in concordance with results obtained by using sealed platinum tubes. They are listed in Table II and are summarized on the phase diagram shown as Fig. 1. Some aspects of these results merit comment and are considered in more detail below.

Phase Analysis at 1623°K

Samples containing between 1 and 5 mole% Ga_2O_3 heated at 1623°K gave X-ray films which showed TiO_2 reflections and reflections which were due to the $Ga_4Ti_{m-4}O_{2m-2}$ oxides (*vide infra*). This was so even in the samples containing only 1 mole% Ga_2O_3. The positions of the rutile lines did not vary from sample to sample as the overall Ga_2O_3 content of the preparations was increased. These were measured for the 1, 2, and 3 mole% samples and the lattice parameters of the rutile cell refined. No significant differences were found between the three results, the mean of which was $a = 0.4579 \pm 1$ nm, $c = 0.2950 \pm 1$ nm which compares favorably with the lattice parameters of the pure TiO_2 starting material which had been heated at 1373°K, viz., $a = 0.4576 \pm 1$ nm, $c = 0.2950 \pm 1$ nm. These results serve to indicate that the classical solid solution region of Ga_2O_3 in TiO_2 is much less than 1 mole% at this temperature, and from an X-ray point of view the region between 1 and 5 mole% Ga_2O_3 is a two-phase one.

Electron microscope examination of samples with nominally 1 or 2 mole% Ga_2O_3 showed that five different microstructures were encountered. At such low Ga_2O_3 compositions fragments were quite frequently found which showed no faulting at all except for occasional dislocations or damage associated with fracture. These gave diffraction patterns which could be interpreted as being due to unchanged rutile. Other very similar fragments were found to contain planar fault boundaries on random {210} planes which appear to be identical to those reported by Gibb and Anderson (*2*). In addition, even in samples containing only 1 mole% Ga_2O_3 crystal fragments were found which were wholly filled with quasi-ordered parallel arrays of these {210} faults. Such fragments are treated here as arising from crystals of the $Ga_4Ti_{m-4}O_{2m-2}$ intergrowth phases and are discussed in more detail below. The number of fragments of this type rapidly increased as the Ga_2O_3 content increased while the number of fragments containing few faults fell to zero for samples containing more than approximately 7 mole% Ga_2O_3.

Between these extreme types of microstructure two other types of crystal fragment were found. The first of these contained essentially isolated {210} faults, but in addition also contained clusters of faults. The spacing across the clusters was in general somewhat wider than the spacing between fault planes in the highest of the homologous series of oxides, $Ga_4Ti_{27}O_{60}$, but of the same order of magnitude, so that these clusters can be regarded as coherent regions of disordered $Ga_4Ti_{m-4}O_{2m-2}$ phases within a rutile crystal. Measurements of the fault spacing within these clusters revealed that in some cases the spacing was narrower at the center of the cluster than

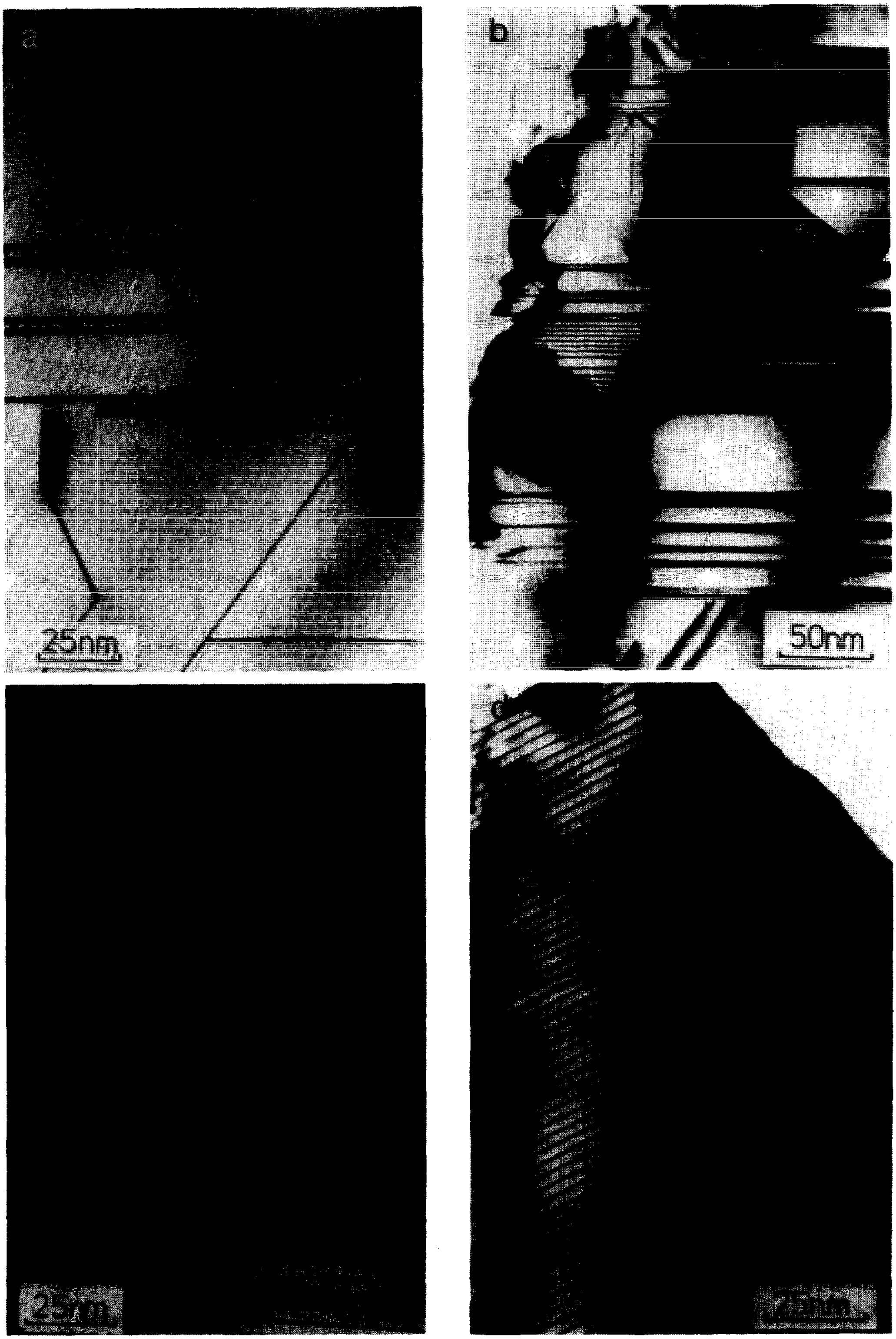

FIGURE 2A–D

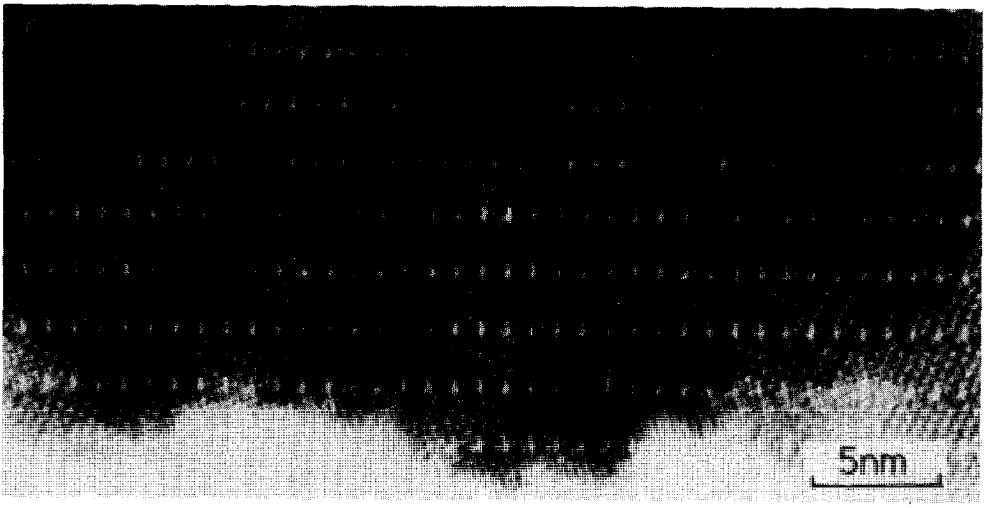

FIG. 2. Electron micrographs showing the typical microstructures found in the TiO_2–Ga_2O_3 system; (a) isolated {210} faults; (b) isolated and clustered {210} faults; (c) disordered parallel array of {210} faults coexisting with regions of rutile structure; (d) partly ordered array of {210} faults forming a disordered crystal of a $Ga_4Ti_{m-4}O_{2m-2}$ oxide; (e) high-resolution electron micrograph of a slightly disordered fragment of a $Ga_4Ti_{m-4}O_{2m-2}$ crystal. The image of the fault planes, revealing prominent tunnels (white spots) is in good agreement with the X-ray structure (*4*).

at the edges, as Bursill and Hyde (*7*) found in slightly reduced TiO_2, while in other cases the spacings seemed to be irregular. This may be due to the mechanism of formation of the fault planes, and will be discussed in more detail in a future communication.

The other type of crystal fragment observed in these samples essentially consisted of $Ga_4Ti_{m-4}O_{2m-2}$ oxides containing reasonably large, coherently intergrown, TiO_2 regions. The spacings between the faults in these regions varied a great deal, and values corresponding to $m \approx 50$ were found. It is possible that larger values would also be encountered. Both of these situations represent steps in a continuous trend in microstructure between TiO_2 and the $Ga_4Ti_{m-4}O_{2m-2}$ oxides. Figure 2 shows this sequence of microstructures.

The trend in microstructures observed in these crystals was paralleled by the electron diffraction pattern sequence found in these samples. Fragments containing a low density of randomly oriented {210} faults gave diffraction patterns similar to that of rutile. As the fault density increased and clusters became apparent streaking along one or several {210} directions became visible and in crystals containing disordered arrays of faults, this streaking was continuous and more intense (Figs. 3a-c).

Samples containing 7.5 mole% Ga_2O_3 or more gave X-ray films which did not show any rutile reflections at all, but indicated solely the presence of the $Ga_4Ti_{m-4}O_{2m-2}$ phases until a gross sample composition of 17.5 mole% Ga_2O_3 was reached, when lines characteristic of Ga_2TiO_5 were also found on the films. The phase range of the $Ga_4Ti_{m-4}O_{2m-2}$ oxides was therefore from about 7.0 to 16.5 mole% Ga_2O_3. The X-ray films from within this range did not, in general, show low angle lines characteristic of the long unit cells of these phases. The most characteristic lines on the photograph were a wide pair centred at about $d = 0.3116$ nm and another doublet centered at about $d = 0.2493$ nm. The separation between the components of each doublet increased as the Ga_2O_3 content of the phases increased, and they are a clear guide as to the presence or absence of the $Ga_4Ti_{m-4}O_{2m-2}$ phases. As sharp, well-resolved low angle lines of good quality were not found on the films obtained from these phases no attempt was made to measure or index the films. For this

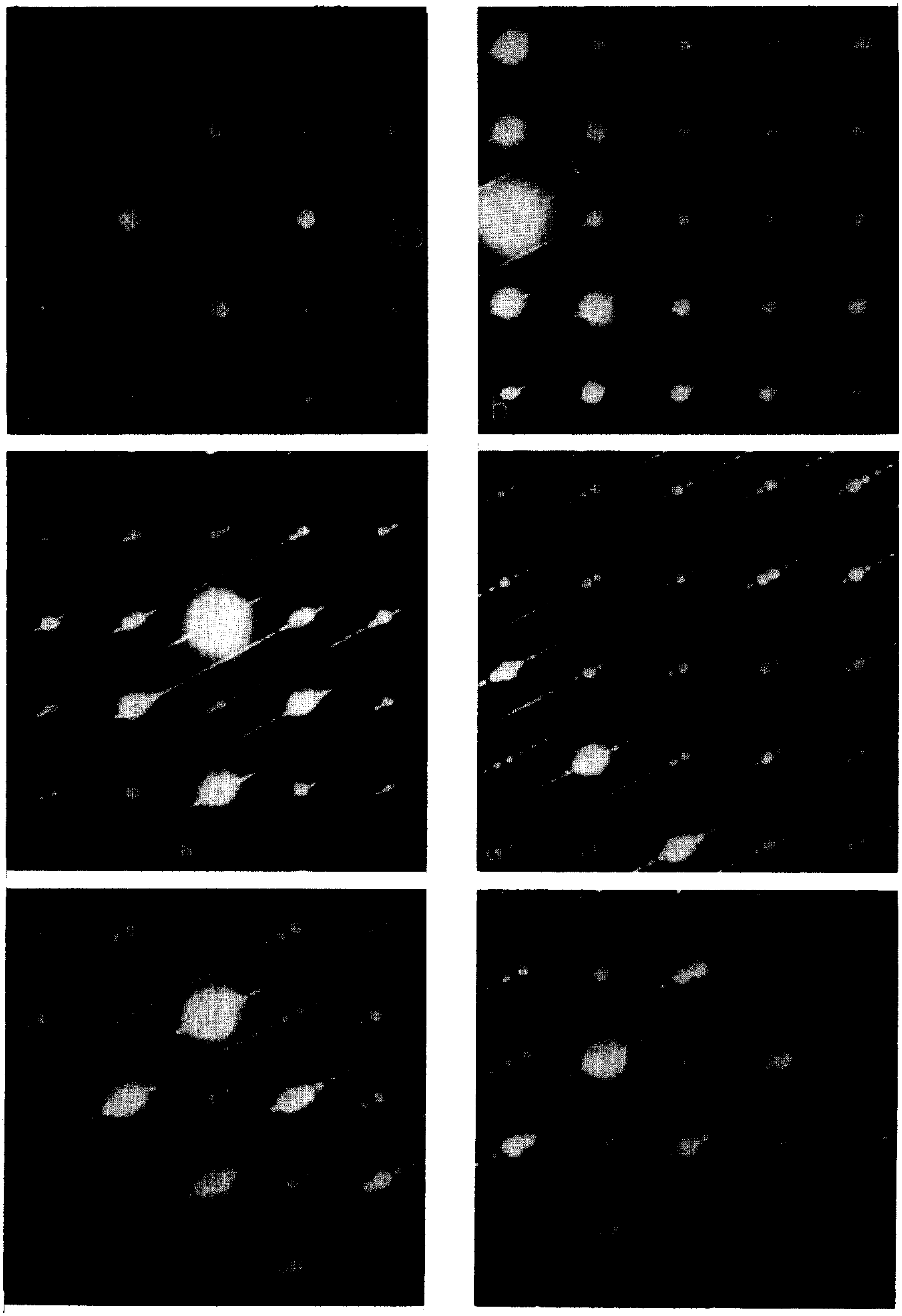

Figure 3A–F

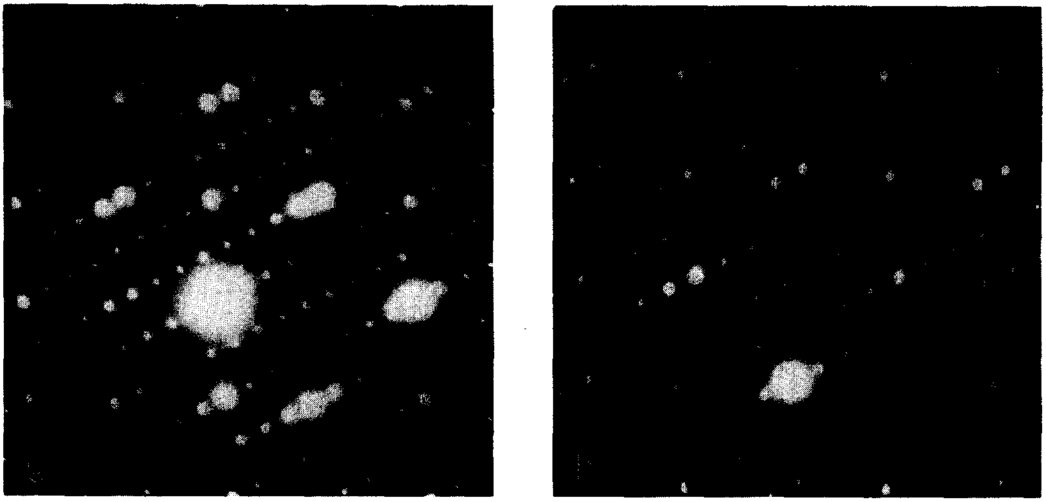

FIG. 3. Electron diffraction patterns found in the TiO_2–Ga_2O_3 system. (a) rutile; (b) rutile containing a few isolated {210} faults; as in Fig. 2a; (c) rutile containing a high density of faults as in Fig. 2c; (d) intergrowth between oxides $n = 14$ and 15, $m = 29$ and 31; (e) intergrowth between oxides $n = 10$ and 11, $m = 21$ and 23; (f) intergrowth between oxides $n = 9$ and 10, $m = 19$ and 21; (g) $Ga_4Ti_{13}O_{32}$, $n = 8$, $m = 17$; $Ga_4Ti_{11}O_{28}$, $n = 7$, $m = 15$.

purpose samples heated for longer periods of time need to be prepared.

The microstructures of samples in the intergrowth phase region were checked by electron microscopy. It was generally found that crystal fragments contained arrays of faults on {210} planes. At the TiO_2-rich side of the phase region these faults were all parallel but the spacings between them were variable and the crystals were visibly disordered (see Fig. 2). These fragments gave rise to diffraction patterns which had heavy streaking along the [210] direction (see Fig. 3). Although this disorder was a common feature of all fragments examined in the $Ga_4Ti_{m-4}O_{2m-2}$ region, the extent of the disorder became less as the amount of Ga_2O_3 increased and as the fault spacings decreased. High resolution electron micrographs of these crystal fragments, such as shown in Fig. 2e, are in agreement with the crystal structures of the oxides as determined by X-ray diffraction (*4*).

As mentioned, at the TiO_2-rich side of the region, electron diffraction patterns were found which showed virtually continuous streaking along the [210] direction, similar to that described above, due to the disorder in the crystals. As the degree of ordering improved, electron diffraction patterns were found in which the streaking was replaced by rows of sharp spots. These superlattice reflections divide the spacing between successive (210) reflections into $(n + \frac{1}{4})$ parts and show that the volume of the crystal giving rise to the diffraction pattern contains well-ordered {210} fault planes separated by $(n + \frac{1}{4})d_{210}$. The relationship between n and m in the formulae of the $Ga_4TI_{m-4}O_{2m-2}$ oxides is simply $n = \frac{1}{2}(m - 1)$ (*2–4*). In practice it was found that the diffraction patterns from samples rich in TiO_2 often consisted of a superposition of several n values, while those on the Ga_2O_3-rich side of the phase region were usually of one n value only, usually $n = 7$ or 8. An examination of these diffraction patterns allowed us to conclude that the limits of the ordered phases were $Ga_4Ti_{29}O_{64}$ ($n = 16$) to $Ga_4Ti_{11}O_{28}$ ($n = 7$). These correspond to metal oxide compositions MO_x of $MO_{1.939}$ to $MO_{1.866}$. At the TiO_2-rich side of the phase diagram, samples containing only 2 mole% Ga_2O_3 contained crystal fragments with well-ordered diffraction patterns, showing n values of 13, 14, and 15 while the sample with 5 mole% showed n

values from 13 to 16. Thereafter, as the Ga_2O_3 content increased, the n values fell, as did their range so that in samples containing 15 mole% Ga_2O_3 only $n = 7$ and 8 were seen, and this was so also for the 17.5 and 20 mole% Ga_2O_3 samples. No other fragments or disordered materials were seen in the samples with more Ga_2O_3.

In samples containing more than about 16.5 mole% Ga_2O_3 X-rays showed that the $Ga_4Ti_{m-4}O_{2m-2}$ phases coexisted with Ga_2TiO_5. There was no detectable change in the lattice parameters of this phase as the overall composition of the samples varied, the values found being $a = 0.9784 \pm 1$ nm, $b = 0.9975 \pm$ nm, $c = 0.3601 \pm 1$ nm for a sample containing 50 mole% Ga_2O_3, and $a = 0.9779 \pm 1$ nm, $b = 0.9972 \pm 1$ nm, $c = 0.3601 \pm 1$ nm for a sample containing 25 mole% Ga_2O_3. These agree reasonably well with the literature data (*8*). The lower stability limit of the Ga_2TiO_5 phase was found to be at 1598 ± 10°K.

Phase Analysis at 1563°K

The results found for these samples were very similar to those at 1623°K and will not be described in detail. The only significant differences were first, that on the Ga_2O_3-rich side of the diagram the $Ga_4Ti_{4-m}O_{2m-2}$ phases were in equilibrium with β-Ga_2O_3 rather than Ga_2TiO_5, and that the phase range of the $Ga_4Ti_{4-m}O_{2m-2}$ phases was narrower than at 1350°K. Electron microscopy showed the phase range to extend from $Ga_4Ti_{13}O_{32}$ ($n = 8$) to $Ga_4Ti_{25}O_{56}$ ($n = 14$) at this temperature. X-ray films showed that there was no significant change in the lattice parameters of either the TiO_2 or β-Ga_2O_3 in equilibrium with these phases. For example, the lattice parameters of β-Ga_2O_3 in a sample containing 50 mole% β-Ga_2O_3 were found to be $a = 1.2311 \pm 1$ nm, $b = 0.3040 \pm 1$ nm, $c = 0.5787 \pm 1$ nm, $\beta = 104.0 \pm 1°$ which compares well with the literature data (*9*) and with X-ray films of the pure β-Ga_2O_3 starting material.

Phase Analysis at 1473°K

The results obtained at this temperature were similar to those found at 1563°K, except that the width of the $Ga_4Ti_{m-4}O_{2m-2}$ phases was only from $Ti_4Ti_{21}O_{48}$ ($n = 12$) to $Ga_4Ti_{25}O_{52}$ ($n = 14$).

Phase Analysis below 1463°K

X-ray analysis of samples heated at temperatures below 1463°K showed only rutile and β-Ga_2O_3 to be present. This was so even in samples heated for 30 days at 1373°K and in samples containing only 1 mole% Ga_2O_3. No other reflections were seen in any of these preparations and from an X-ray viewpoint the phase region appears to contain two coexisting stoichiometric phases. The X-ray films of samples heated at 1373°C containing 1, 2, and 3 mole% Ga_2O_3 were measured and the rutile lattice parameters calculated. No significant variation was found in the values between any of these samples, and the mean values, $a = 0.4577 \pm 1$ nm, $c = 0.2949 \pm 1$ nm, were not significantly different from those obtained by measuring an X-ray film of the starting TiO_2 (*vide supra*). This indicates that any solid solution of Ga_2O_3 in TiO_2 in the classical sense is very small, and much less than 1 mole% at this temperature.

Electron microscope examination showed that crystal fragments were of three types, unfaulted rutile, rutile containing a few isolated faults lying on $\{210\}$ planes and β-Ga_2O_3. The TiO_2 and β-Ga_2O_3 were not studied in any detail. The faulted crystals were found in roughly the same proportions in all samples on the TiO_2-rich side of the phase diagram. Their appearance did not change significantly either in samples heated for longer times or as the nominal Ga_2O_3 content of the samples varied. Figure 2a shows a typical example of this faulted material. The diffraction patterns of the faulted material are similar to that of rutile, although streaking along one or more of the

{210} directions was sometimes seen when the fault density was relatively high.

In order to check whether the phase boundary at 1463°K was genuine and not merely a reflection of kinetics, samples containing only intergrowth phases which had been prepared at 1623 were heated at 1373°K. In these experiments the material was heated in sealed silica ampoules, as heating in air only resulted in a material loss of Ga_2O_3 from the system. These experiments showed that the intergrowth oxides decomposed, although very slowly, to rutile and β-Ga_2O_3 under these conditions, and confirmed that the 1463°K-line was a phase boundary.

Discussion

The results show that at temperatures of the order of 1373–1423°K only a very small amount of Ga_2O_3 can be taken into the rutile lattice and that it is accommodated as slabs of β-Ga_2O_3 coherently intergrown in the TiO_2 crystals. At temperatures below 1462°K the degree of aggregation of these lamellae is small and their total density low. In terms of powder X-ray diffraction, the matrix consists largely of unaltered rutile, so that although certain X-ray reflections may be broadened somewhat the lattice parameter of the rutile phase does not change significantly.

At temperatures above 1463°K the amount of β-Ga_2O_3 able to enter the rutile structure increases substantially. The reasons for this have not been resolved in the present study, but may be connected with the expansion of the TiO_2 lattice at higher temperatures or with the increased vapor pressure of β-Ga_2O_3. The experiments show, however, that above this temperature isolated fault lamellae begin to aggregate into clusters and to produce larger volumes of ordered or partly ordered faults. The reasons for the aggregation of the faults into clusters in the 1–7 mole% Ga_2O_3 region is essentially a problem of mechanism, and will be discussed in more detail in a future paper. There would appear to be a continuous range of microstructures between TiO_2 and ordered arrays of faults which are found at about 7.5 mole% Ga_2O_3. Because of this behavior, the phase boundary between TiO_2 and the $Ga_4Ti_{m-4}O_{2m-2}$ intergrowth phases is somewhat artificial in nature. The position shown in Fig. 1 marks where our X-ray diffraction patterns showed no rutile reflections rather than the presence of only a single well-ordered phase of composition $Ga_4Ti_{27}O_{60}$. In general, on this basis, the boundary between TiO_2 and the intergrowth phases would not be expected to vary greatly with temperature, as has been found.

In our studies the intergrowth phase region on the phase diagram is a nonstoichiometric region, as the fault lamellae were never well enough ordered to give a set of X-ray powder patterns corresponding to discrete $Ga_4Ti_{m-4}O_{2m-2}$ oxides. The interaction between the faults appears to be low and high temperatures and long annealing times seem to be necessary to produce true equilibrium in this part of the phase diagram. Unless this is done, the whole phase region from TiO_2 to the gallia-rich side of the $Ga_4Ti_{m-4}O_{2m-2}$ oxides forms a region of variable composition in which changes in the anion to cation ratio are brought about by coherent intergrowth of lamellae of β-Ga_2O_3.

The gallia-rich side of the intergrowth phase region was characterized by noting the presence or absence of other phases, either β-Ga_2O_3 or Ga_2TiO_5, on the powder X-ray diagrams. The increasing width of the intergrowth phase region as the temperature increases is indicative of the increased tolerance of the TiO_2 lattice to the β-Ga_2O_3 structure. Although the gallia-rich phase which is in equilibrium with these intergrowth oxides changes from β-Ga_2O_3 below 1608°K to pseudo-brookite, Ga_2TiO_5, above this temperature, there does not seem to be any marked effect upon the width of the intergrowth phase region. Our present results suggest that neither β-Ga_2O_3 nor Ga_2TiO_5 are able to form solid solutions with the intergrowth phases, but further studies are needed to check this suggestion.

The microstructures occurring at higher temperatures are of some interest. In both the Fe–Ti–O and Cr–Ti–O ternary systems high-temperature phases exist which are different from those found at temperatures of the order of 1600°K (*10, 11*) and the same may be true in the Ga–Ti–O system. Experiments (to be reported elsewhere) have shown that the intergrowth phases can be melted in the beam of the electron microscope and that under these conditions they seem to be stable up to their melting points. The conditions used in such experiments are, however, far from equilibrium, and need to be checked by experiments under controlled conditions. In addition, the way in which the rutile structure varies as the composition of the solid changes from the fully oxidized TiO_2–β-Ga_2O_3 line to the reduced TiO_2–Ti_2O_3 line is of considerable interest. These questions are to be the subject of future research studies.

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