

An investigation of phase stability in the Y_2O_3 - Al_2O_3 system

J. S. ABELL, I. R. HARRIS

Department of Physical Metallurgy and Science of Materials, University of Birmingham, UK

B. COCKAYNE, B. LENT

Royal Radar Establishment, Malvern, Worcs, UK

The stability of the three known phases in the Y_2O_3 - Al_2O_3 pseudo-binary system has been investigated. $YAlO_3$ (YAP) and $Y_4Al_2O_9$ (YAM) decompose at elevated temperatures, the products of the reaction being the third compound $Y_3Al_5O_{12}$ (YAG) and an unknown phase (designated X). The decomposition is most evident in powders but can also be initiated on the surface of bulk single crystals. X-ray diffraction studies have been performed in an attempt to identify the structure and composition of the unknown phase. The thermal decomposition has been found to be surface controlled and an optical and scanning electron microscope study of the associated morphological changes in $YAlO_3$ indicates that the reaction involves localized surface melting, probably with the loss of oxygen which effectively moves the composition off the binary join.

1. Introduction

Considerable doubt exists about the precise form of the equilibrium phase diagram for the pseudo-binary system Y_2O_3 - Al_2O_3 , particularly for those parts of the system which include the compounds $Y_3Al_5O_{12}$ and $YAlO_3$ which are of considerable interest as solid state laser materials [1]. There are three reported congruent phases in the system, occurring at the Y_2O_3 : Al_2O_3 ratios of 3:5 (YAG), 1:1 (YAP) and 2:1 (YAM). YAG adopts the cubic garnet structure [2] and is the only unambiguously stable phase in the system. YAP has an orthorhombic, distorted perovskite structure [3] and has generally been regarded as a metastable compound [4-7]. Toropov *et al* [4] suggested that YAP formed peritectically from the 2:1 compound and liquid at 1875°C but had a limited range of stability, decomposing into the two neighbouring compounds, YAM and YAG, at 1835°C. Quenching from within this range in an attempt to produce a homogeneous single phase sample proved difficult; a metastable two-phase equilibrium between YAG and YAM was more often established. Warshaw and Roy [5] stated that YAP was always metastable and did not record it on the phase diagram. No reaction was observed at low temperatures, but above

1100°C reaction occurred slowly, the products being YAG and YAM. More recently, however, the phase diagram of Mizuno and Noguchi [6] has shown YAP as a congruent melting compound, which is unstable below 1600°C. YAP single crystals have been grown and cooled to room temperature [8-10] which also lends support to the congruent nature of this compound. However, the metastability of this phase in powdered form has recently been reaffirmed by X-ray diffraction studies [7], with extensive thermal decomposition occurring at temperatures in excess of 1300°C; the products of the reaction were found to be YAG and an unidentified phase (designated X) and not YAG and YAM as previously suggested [4, 5].

YAM is thought to have a monoclinic structure and is also reported to melt congruently [4-6]. Single crystals can be grown [11], but they crack extensively on cooling to 1000°C; this behaviour may be associated with the reported instability [5, 12] or a polymorphic transition [4] for the compound in this temperature range.

Experiments reported here confirm that YAM is unstable and decomposes under similar conditions to YAP, the products being YAG and X. Further experiments have been undertaken

to identify the structure and composition of this new phase and to assess its relevance to the existing phase diagram. These experiments have also provided information on the mechanism of the thermal decomposition of YAP and this aspect has been further studied by optical and scanning electron microscopy.

2. Experimental techniques and materials

Room temperature X-ray powder diffraction patterns were recorded on a standard 114 mm diameter camera using $\text{CoK}\alpha$ radiation. High temperature patterns were taken using a Materials Research Corporation furnace attachment to a Philips diffractometer which has been described in detail elsewhere [13]. Heat-treatments up to 1600°C were performed mainly in air on Netzsch DTA equipment in a silicon carbide furnace. Anneals at higher temperatures were carried out on a small dished iridium resistance heater surrounded by MgO refractory [11]. An argon atmosphere was usually employed although an argon/hydrogen mixture was used in the experiments to be described in Section 3.5. This strip heater was also used to prepare the melts referred to in Section 3.3. Surface morphologies were studied using a Zeiss Ultraphot II optical microscope and a Cambridge S4 scanning electron microscope (SEM). A carbon or gold/palladium coating was evaporated on to the SEM specimens to prevent charging and consequent beam deflection.

Both powdered and single crystal material were used in the investigation. Of the component oxides, Y_2O_3 and Nd_2O_3 were supplied by Rare-Earth Products Ltd, and the Al_2O_3 by BDH Ltd. Powders of the three compounds YAG, YAP and YAM were obtained by crushing Czochralski-grown single crystal material and powders of intermediate composition were obtained from melts prepared on the iridium strip heater. The surface studies were performed on the as-grown surfaces of Czochralski-grown YAP single crystals and on slices cut perpendicular to the growth axis (a , b or c of the orthorhombic structure) and mechanically polished with Syton.

3. X-ray diffraction studies in the Y_2O_3 - Al_2O_3 system

3.1. Thermal decomposition of YAP

In powdered form YAP decomposes to produce YAG and X at temperatures between 1300 and

1800°C . The reaction is a slow one depending on the time and temperature of the heat-treatment and complete decomposition into YAG plus X has not been achieved by a simple anneal; residual X-ray diffraction lines from the initial YAP structure can always be detected. The reaction kinetics are strongly dependent on the surface to volume ratio of the sample and in the bulk crystal no X-ray evidence for decomposition has been observed. In particular, bulk single crystal material, when annealed for 2 h at 1820°C in air and then crushed at room temperature, showed no sign of decomposition. This temperature is close to the melting point of the compound (1875°C) and is in the reported stability range for this phase. However, when YAP powders, previously decomposed into predominantly YAG and X, were similarly annealed, the only detectable change in the room temperature pattern was a reduction in intensity and an increased "spottiness" of the remaining YAP lines. No reversion to a simple YAP pattern, expected if this temperature lay in the stability range, had taken place. Such a reversion was only achieved by re-melting the decomposed powder in an oxidizing atmosphere.

3.2. Thermal decomposition of YAM

Single crystals of YAM can be grown by the Czochralski method [11]. However, when the transparent crystal is cooled subsequent to growth, it turns opaque at approximately 1000°C . Room temperature examination showed that this opacity is due to small cracks in the bulk of the material. Optical measurements by Toropov *et al* [4] suggest the occurrence of a polymorphic transition at approximately 1000°C , but other workers suggest that the phase actually decomposes below this temperature [5, 12]. Extensive cracking in the present material precluded a single crystal dilatometric investigation of the high temperature structural properties of this phase in a similar manner to that performed on YAP [10]. The work was, therefore, confined to X-ray studies on the phase stability of YAM powder.

The X-ray powder diffraction pattern recorded on a melt of the YAM composition was in good agreement with earlier work [4, 5, 14]. No YAP or YAG reflections were observed. Samples heat-treated in air for up to 24 h at temperatures in excess of 1400°C showed significant changes in the subsequent room temperature diffraction pattern. Reflections from the initial YAM phase

TABLE I Observed interplanar spacings and relative intensities of YAM in the as-crushed and annealed state compared with those of YAG, and the unknown phase X derived from the decomposition of YAP [7]. Note that some of the YAM lines appear spotty (s) after the anneal

YAM				YAG, as-crushed			Unknown phase X	
As-crushed		2 h 1400°C		<i>hkl</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>
7.452	ms	7.401 (s)	ms					
5.260	w	5.249	vw					
		4.909	vw	211	4.897	s		
4.714	ms	4.704 (s)	ms					
4.555	w	4.541	vw					
4.199	vw							
		4.035	vw					
3.714	w	3.702	vw				4.047	w
3.335	m	3.330 (s)	ms					
		3.205	vw	321	3.207	ms		
		3.105	vw				3.110	mw
3.017	vs	3.010 (s)	vs	400	3.000	ms		
2.919	s	2.910 (s)	s					
		2.786	m				2.788	mw
		2.734	w				2.732	mw
		2.681	m	420	2.682	vs		
2.616	w	2.611 (s)	m					
2.564	mw	2.551 (s)	m					
2.526	m	2.521 (s)	m					
2.470	mw	2.461	m	422	2.446	ms		
2.283	mw	2.280	m					
		2.189	w	521	2.190	ms		
2.066	m	2.061 (s)	ms					
2.045	mw	2.044	w					
1.979	vw	1.978	vw					
		1.946	w	611	1.946	ms		
		1.921	vw				1.921	mw
1.903	vw							
1.843	mw	1.840 (s)	mw					

still formed the predominant part of the pattern but several extra lines were detected. Many of these corresponded to YAG and no reflections from YAP were detected. Table I compares the low angle *d*-spacings and relative intensities of the as-crushed starting material and a heat-treated sample with those of YAG and X; only the strongest YAG lines have been observed, but for those the agreement is excellent. The additional lines can be attributed to the strongest lines of the phase X, involved in the YAP decomposition [7]. Thus, the products of the phase separation of YAM and YAP appear to be identical.

The reaction in YAM is more sluggish than in YAP since similar treatments produce less of the product phases. As in YAP, the reaction kinetics

were dependent on the surface to volume ratio since the bulk starting material was single phase, other phases only being detected after powdering and heat-treatment. After annealing, many of the residual YAM lines were discontinuous or "spotty" in nature; this feature will be further discussed in Section 3.6.

3.3. Structure of intermediate compositions

In an attempt to establish the nature of X, melts at intermediate compositions across the pseudo-binary system were prepared by heating mixtures of Y_2O_3 and Al_2O_3 in the appropriate proportions on the iridium strip heater. The compositions used and a summary of the results of these experiments are contained in Table II. The corresponding behaviour of the three

TABLE II Phases detected by X-ray diffraction in melts of various compositions in the pseudo-binary $Y_2O_3:Al_2O_3$ system at room temperature, both in the as-crushed and heat-treated states, and at elevated temperature. The phases YAG, YAP and YAM are abbreviated to G, P and M respectively and the phases present are given in order of predominance

Composition $Y_2O_3:Al_2O_3$	Phases at room temperature		Anneal conditions	Phases up to $T^\circ C$
	As-crushed	After anneal		
YAG 37.5 : 62.5	G	G	2 h, 1600°C	G 1500
1 45 : 55	G + P	G + X + P (4 lines)	2 h, 1600°C	G + P 1380
YAP 50 : 50	P	G + X + P	2 h, 1600°C	P + G + (X) 1500
2 55 : 45	P + M	P + M + G (3 lines)	2 h, 1600°C	P + M 1460
3 60 : 40	M + P	M + P + G (1 line)	2 h, 1600°C	M + P 1500
4 65 : 35	M + P	M + P + G (1 line)	2 h, 1600°C	M + P + G 1510
YAM 66.7 : 33.3	M	M + G + X (1 line)	2 h, 1600°C	M + G 1500
5 70 : 30	M + Y_2O_3	M	19 h, 1500°C	M + Y_2O_3 1425
6 75 : 25	M + Y_2O_3	M + Y_2O_3	19 h, 1500°C	M + Y_2O_3 1525

compounds YAG, YAP and YAM are included for comparison. These results show no evidence of X in the as-crushed room temperature diffraction patterns of the various melts. They all exhibited two-phase patterns consistent with the existing phase diagrams [4, 6]. This is illustrated schematically in Fig. 1. If X lies on the Y_2O_3 - Al_2O_3 binary section, it would be expected to occur at the Y_2O_3 -rich end of the system since the decomposition of both YAP and YAM involves YAG and X, but melts in this region show only YAM plus Y_2O_3 .

3.4. Heat-treatment of intermediate compositions

The information obtained from the diffraction patterns of the annealed material is also shown in Table II. Decomposition occurred in all the melts containing YAP as one of the constituents (compositions 1 to 4) but the extent of the decomposition among these melts decreased with increasing Y_2O_3 content and X was only observed in melt 1, YAP and YAM. The proportion of YAG produced must decrease with increasing Y_2O_3 content, according to the lever rule, but the observed absence of X from the decomposition of melts 2 to 6 is inconsistent with the simple application of this rule to the pseudo-binary join. The heat-treatments of melts 2 to 4 suggest that the YAP plus YAM mixture is more stable than the individual phases. The result of an extended anneal of composition 5 suggests that YAM can absorb excess Y_2O_3 , indicating that this phase has a small range of homogeneity and should not be represented by a line compound on the phase

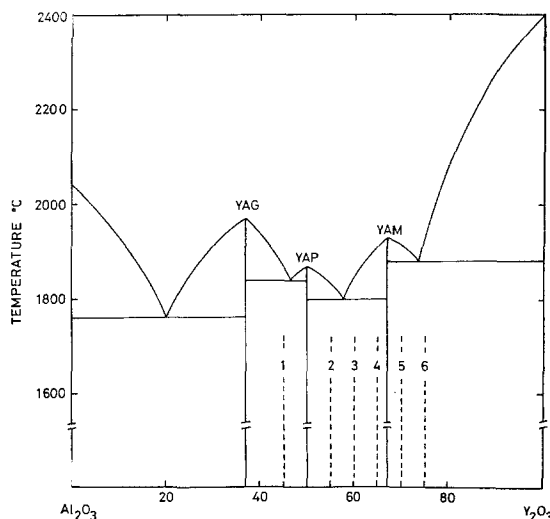


Figure 1 Schematic phase diagram for the Y_2O_3 - Al_2O_3 system showing the three reported compounds, YAG, YAP and YAM together with the compositions whose structure have been studied and summarized in Table II.

diagram. The high temperature X-ray results on the various intermediate compositions reveal that the room temperature two-phase patterns are stable up to temperatures in the region of 1450°C as indicated in Table II. The results were thus consistent with the behaviour of the heat-treated powders.

Attempts to correlate these experimental data with various hypothetical phase diagrams which include X on the pseudo-binary join have proved unsuccessful. A possible explanation is that, during the prolonged anneals, a loss of one

or more of the constituents in the system occurs; such a loss would effectively move the overall composition off the Y_2O_3 - Al_2O_3 pseudo-binary join. Since one of the products is YAG, this would imply that the composition of X does not lie on this join. If this loss occurs very slowly, which would be consistent with the observed sluggishness of the decomposition in YAP and YAM powders, no significant change in overall composition would arise in the rapidly cooled melts and the resultant room temperature structure would not be affected. Only after subsequent annealing of the powdered melts would the decomposition occur. Of the elements constituting this ternary system the most likely candidate for such behaviour would be oxygen. Such a reaction would be very dependent on surface to volume ratio and could explain the difference in behaviour of bulk and powdered YAP [7].

3.5. Effect of atmosphere on YAP decomposition

To test the possibility of oxygen loss, two samples of YAP powder were heat-treated in a reducing atmosphere (A/H_2), one for 5 days at $1300^\circ C$ and the other for 100 h at $1600^\circ C$. The diffraction pattern of the first sample showed only the YAP structure and revealed no evidence of YAG or X, indicating that the reducing atmosphere did not enhance the decomposition at this temperature, which is at the lower end of the observed decomposition range [7]. However, the second sample decomposed to give a three-phase diffraction pattern of YAG, YAP and X, in order of predominance. The proportion of X was equivalent to that found after anneals at temperatures above $1700^\circ C$ in a non-reducing atmosphere [7]. No additional diffraction data on this new phase were, therefore, obtained from

these experiments and no significant change in the reaction kinetics was achieved by introducing a reducing atmosphere during the anneal. This observation is consistent with the lack of dependence on prevailing environment (argon or vacuum) found during the previous X-ray diffraction studies [7].

3.6. Skin effect in YAP decomposition

A close examination of the diffraction patterns of the decomposed powders revealed that the lines corresponding to the residual YAP phase were invariably spotty in nature, whereas those of the product YAG and X phases were usually continuous. This suggests either that the YAP crystallite size increased during the anneal or that the YAP grains were being partially concealed from the X-ray beam by a surface layer of the decomposition products.

The existence of a surface layer was confirmed by the following series of experiments. A powdered sample of YAP with a characterized diffraction pattern was heat-treated in air for 2 h at $1500^\circ C$ and furnace cooled before recording the pattern again. The sample was then finely ground to break up any skin formed during the anneal and a further diffraction pattern obtained. This sequence was repeated four times on the same sample and the results are summarized in Table III.

The predominant phase present after the first anneal was YAG; the intensities of the YAP lines decreased and many became discontinuous in nature, in contrast to the YAG and X lines. After grinding, the YAP lines were no longer spotty and in many cases the line intensities had increased significantly. A particular example is the (200) reflection which disappeared after the anneal, and was again detected on grinding the sample. At the same time, the intensities of

TABLE III A summary of the phases detected and comments on the nature of the X-ray diffraction patterns during successive annealing and grinding procedures performed on a YAP powder sample. Anneals were carried out in air for 2 h at $1500^\circ C$. The phases YAG and YAP are abbreviated to G and P respectively and the phases are given in order of predominance

Treatment	Resultant phases	Comments
1. Anneal	G + X + P	P lines discontinuous
2. Ground	G + P + X	P lines continuous. Some G + X intensities reduced
3. Anneal, ground	G + X	Grinding necessary due to sintering
4. Anneal, ground	G + X	Additional lines
5. Anneal, ground	G + X	Some X intensities reduced

many of the YAG and X lines were reduced. Thus, the relative proportions of the three phases as detected by the X-rays had been changed by grinding the reacted powder. Hence, the decomposition of YAP takes place at the particle surface producing a skin containing the phases YAG and X.

The YAP exposed by grinding at stage 2 (see Table III) decomposed on further heat-treatment. The powder sintered after this second anneal and further grinding was necessary before the diffraction pattern could again be recorded. After this anneal (stage 3) no YAP lines were detected and complete decomposition to YAG and X had apparently occurred. However, this is not the terminal stage of the decomposition because on repeating the procedure (stage 4) additional lines were observed and several of the lines corresponding to X were reduced in intensity and, in some cases, had disappeared. Similar results were obtained in a previous study [7] on increasing the anneal temperature from 1600 to 1800°C. In both cases the extra lines were not attributable to the known compounds in the $Y_2O_3-Al_2O_3$ system.

A similar experiment on YAM powder samples showed the same type of behaviour. The spotty nature of the residual YAM lines after heat-treatment has already been mentioned (see Section 2 and Table I). Grinding of the reacted powder again produced continuous lines but total elimination of the YAM structure by the annealing and grinding procedure outlined for YAP proved impossible. This is consistent with YAM being a more stable compound than YAP and higher temperature anneals are presumably required to achieve complete decomposition.

There exists good agreement between the d -spacings of the unindexed lines occurring in this series of experiments and those observed previously [7], but sufficient data on this phase have not yet been accumulated to enable any structures to be determined. These experiments have shown, however, that the thermal decomposition in YAP, and most probably in YAM, takes place at the surface and probably involves a constituent loss which effectively moves the resultant composition off the $Y_2O_3-Al_2O_3$ pseudo-binary join.

4. Surface studies on YAP

4.1. Powdered material

The surface morphology of powdered samples of YAP in the as-crushed and heat-treated con-

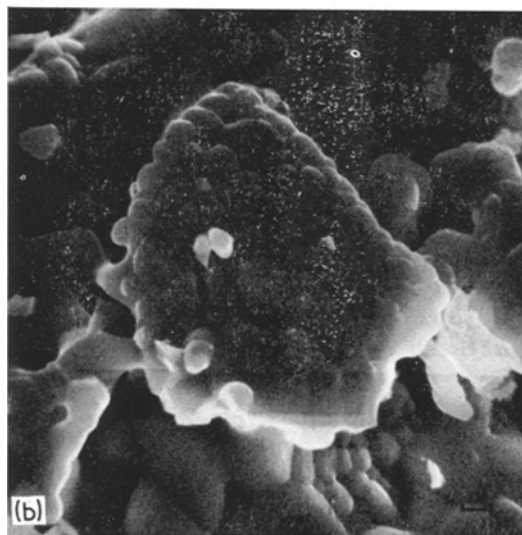
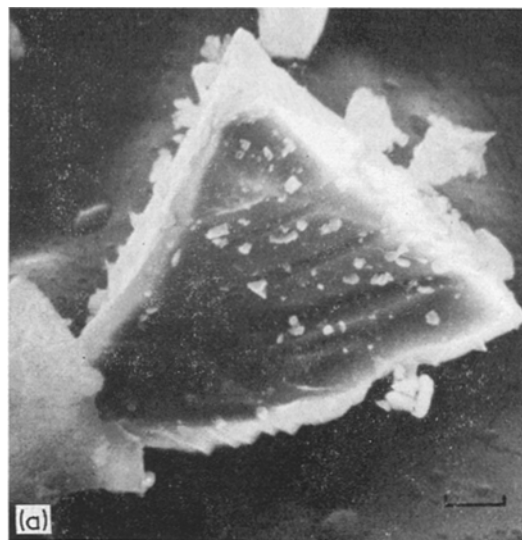


Figure 2 SEM photograph of YAP powder (a) as-crushed and (b) heat-treated for 415 min at 1590°C (marker = 1 μ m).

dition were examined in the scanning electron microscope (SEM). Typical photographs of a particle surface in the two states are shown in Fig. 2. The difference in appearance is quite marked. In the as-crushed state the particles showed the sharp angular edges and surface markings characteristic of brittle fracture. After heat-treatment, however, the edges and corners were considerably smoother and the surface features adopted a cellular structure. This

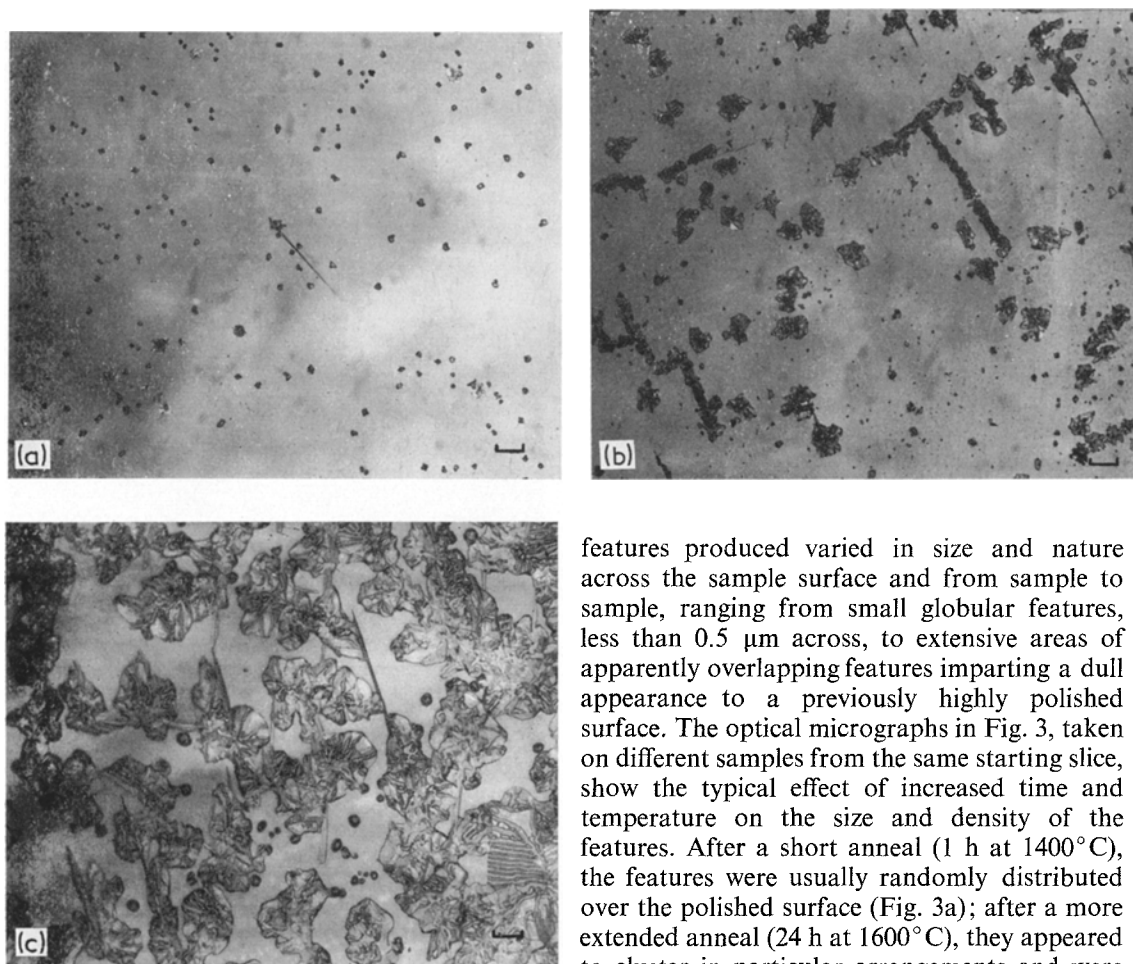


Figure 3 Optical micrographs of the polished surface of a YAP *c*-slice after (a) 1 h at 1500°C, (b) 2 h at 1500°C and (c) 24 h at 1570°C (marker = 20 μ m).

constitutes further evidence that the thermal decomposition in this material involves a surface reaction which results in the formation of a skin at high temperatures. The overall appearance of the heat-treated material gave the impression that melting had occurred. A similar though much less marked behaviour has been observed on YAM powder samples.

4.2. Single crystal slices

An optical and SEM comparison of the surfaces of as-polished and subsequently annealed slices of single crystal YAP provided further confirmation of a surface reaction occurring in this material. As a result of the heat-treatment, a pronounced surface structure developed. The

features produced varied in size and nature across the sample surface and from sample to sample, ranging from small globular features, less than 0.5 μ m across, to extensive areas of apparently overlapping features imparting a dull appearance to a previously highly polished surface. The optical micrographs in Fig. 3, taken on different samples from the same starting slice, show the typical effect of increased time and temperature on the size and density of the features. After a short anneal (1 h at 1400°C), the features were usually randomly distributed over the polished surface (Fig. 3a); after a more extended anneal (24 h at 1600°C), they appeared to cluster in particular arrangements and were conspicuous at the surface edges as seen in Fig. 3c. This dependence on the particular heat-

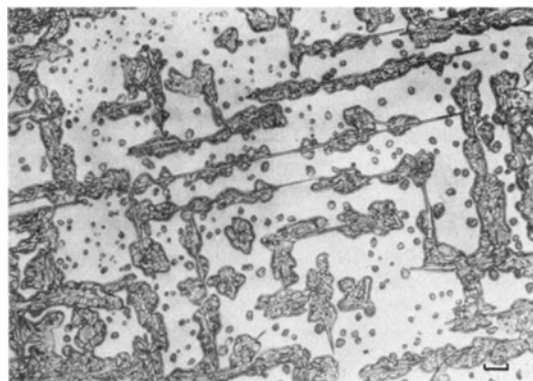


Figure 4 Optical micrograph of the polished surface of a YAP *a*-slice after 24 h at 1570°C showing the crystallographic configuration of growth features (marker = 20 μ m).

treatment was consistent with the results of the X-ray studies where the extent of the decomposition was found to increase in a similar manner.

The linear markings joining or running into some of the features were noticeable on most samples and were usually parallel to one or two directions in the surface. Growth during further heat-treatment usually occurred preferentially along these linear markings with the result that the features appeared to adopt a crystallographic configuration. This behaviour can be seen at an early stage in Fig. 3b and at a later stage in Fig. 4. The small globular features are clearly seen interspersed within the apparent crystallographic arrays. Chemically polishing the sample in phosphoric acid at approximately 400°C showed that the growth features were confined to the surface; a few minutes of this treatment removed the features which could be reproduced by a further high temperature anneal.

A further example of this surface structure on a previously polished slice is shown in the SEM photograph of Fig. 5 where the original fine scratches resulting from the mechanical polish can still be seen. Most of the features appear to be located in depressions formed in the original surface. Many of them exhibit irregular surfaces and boundaries. Others are definitely crystallographic in nature, as typified by Fig. 6, which shows a partially faceted growth feature; the surrounding surface depression can be clearly seen. The irregular features are particularly prevalent at the corners between two faces, as seen in Fig. 7. Some of the original fracture markings can still be seen on the broken edge of the sample but most of them have been removed by growth of the features. The extent and irregularity of the surface characteristics is particularly marked on these exposed edges and is probably related to the stress concentrations associated with such regions; such a view is supported by the frequent observation of rows of features parallel to pre-existing surface scratches. The size and density of these features also depends on the orientation of the crystal slice. Thus, an examination of the polished surfaces of slices cut perpendicular to the *a*-, *b*- and *c*-axis, annealed under the same conditions, showed that the features were most prominent on *a*-slices and least on *c*-slices. Comparable observations on a polished single crystal slice of YAG annealed in air for 12 h at 1600°C showed no evidence of decomposition.

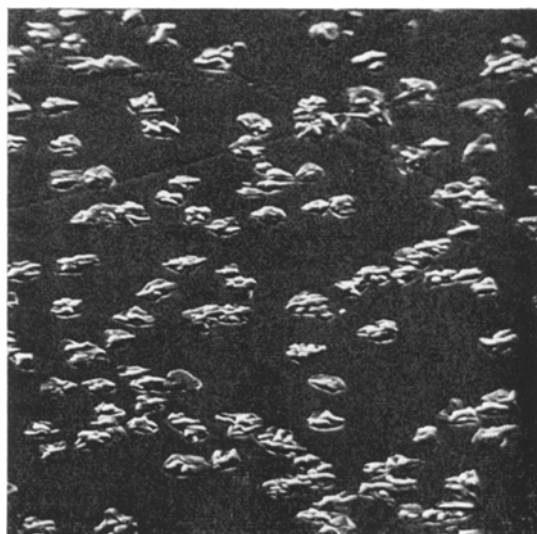


Figure 5 SEM photograph of the polished surface of a YAP *a*-axis slice after 20 h at 1400°C (marker = 10 μm).

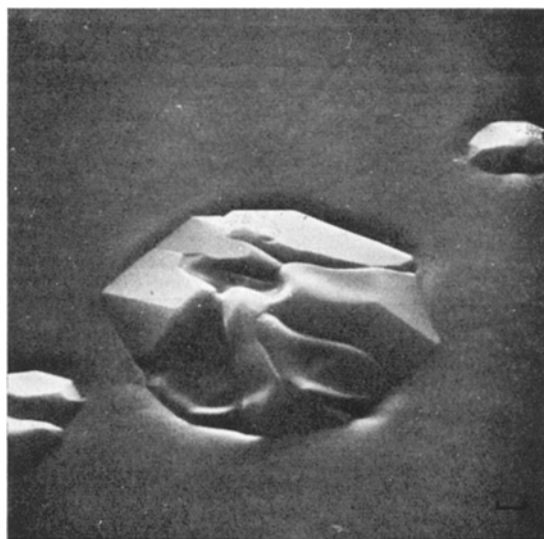


Figure 6 SEM photograph of a faceted growth feature on a polished *b*-axis slice of YAP after 77 h at 1520°C (marker = 1 μm).

4.3. As-grown surfaces

The observations so far described have been made on material powdered or sliced from single crystals and subjected to a high temperature anneal. However, the as-grown single crystal experiences very similar anneal conditions immediately after solidification until it is cooled

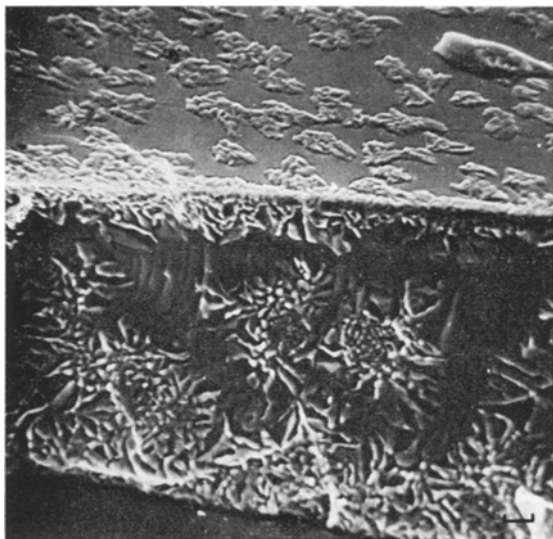


Figure 7 SEM photograph of the top (polished) and side (fractured) faces of a YAP *b*-axis slice after 77 h at 1520°C (marker = 10 μ m).

to low temperatures subsequent to growth. A typical time at high temperature is 24 h and so extensive growth features would be expected to occur on the surface of as-grown crystals.

Optical and SEM examination of various sections of an as-grown crystal surface showed very few surface markings characteristic of the decomposition. On only one of the sections examined were features observed resembling those already described, and these were confined to a small area on an otherwise plain surface. This area is shown in Fig. 8a. It should be noted from the magnification that these features are very fine indeed compared with those seen previously on annealed slices. It is not yet known whether these markings are definitely related to the decomposition features.

If these as-grown surface sections are subjected to anneals similar to those described in the previous section, then the familiar growth features readily develop. This is illustrated in Fig. 8b which is taken on the same surface as Fig. 8a after a 24 h anneal in air at 1550°C. The features were mainly of the rounded rather than faceted type and were particularly prevalent on the surface ridges.

5. Melting point determinations

During the course of the present work, the melting points of the three congruent phases

YAG, YAP and YAM have been determined. The melting point of YAG was confirmed at 1970°C using Ir/Ir-Rh thermocouples and the melting points of the other two phases were measured by optical pyrometry using a YAG melt as a standard. A comparison of previous data with present values is shown in Table IV. Fairly good agreement exists in the values for YAG except for that of Yoder and Keith [2]. Their claim of a solid state reaction occurring in their composition at 1970°C was attributed by Warsaw and Roy [5] to the formation of YAP from the melt which then transformed into YAG at 1970°C. Later work has proved this to be incorrect since consistent values of the melting point of YAP have been observed at the considerably lower value of 1870°C. Where the present melting points do depart significantly from previous work is for YAM where a value of 1930°C was obtained, which is approximately 100°C lower than reported earlier.

6. Discussion and conclusions

Substantial evidence has been presented to show that the thermal decomposition of YAP, and most probably YAM, is surface controlled. A surface layer consisting of the decomposition products, YAG and X, forms after an extended heat-treatment. The morphology of the features observed by SEM on the surface of polished slices of YAP indicates that they correspond to areas of the sample that have been molten at elevated temperature. The surface depression associated with these regions confirms that growth from the melt is responsible for the features. Alternative growth mechanisms, such as solid state transformations, would only produce a highly crystallographic surface structure without an associated depression. Similarly, if vapour growth was responsible, no surface depression would be necessary and the features would form on the smooth substrate crystal surface; thermal etching would produce only a surface pit with no protruding structure.

The initial stage in the reaction appears to be the formation of surface globules which are observed after a short anneal. On increasing the anneal time or temperature, these globules grow by absorbing material from the surrounding flat surface, thus creating a surface depression. In some cases they solidify on cooling to produce the small faceted features typified by Fig. 6. In other cases, neighbouring globules coagulate and eventually form pools of molten material which

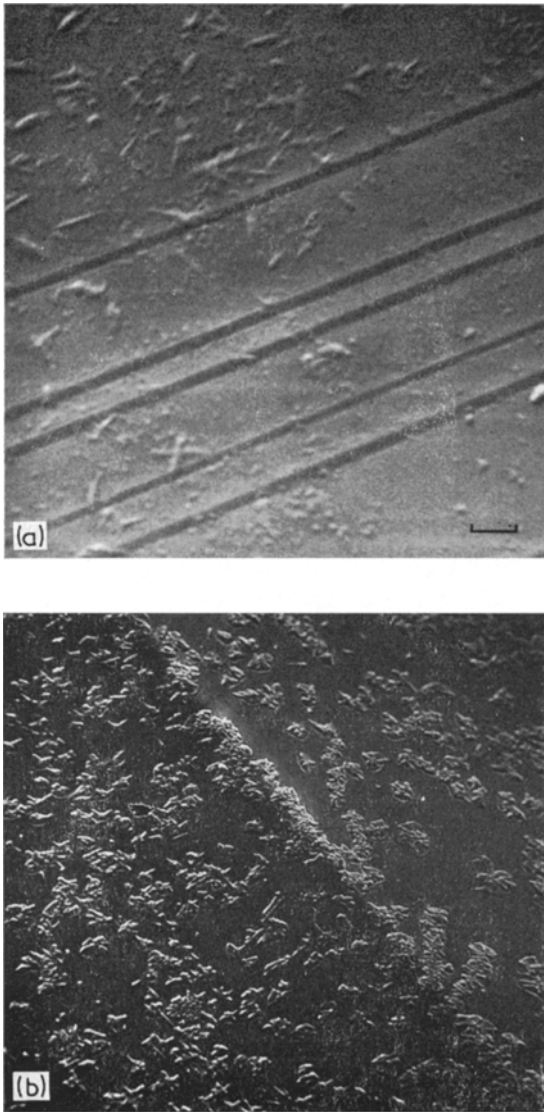


Figure 8 SEM photograph of (a) an as-grown surface of a YAP single crystal (marker = 1 μm) and (b) the same surface after 38 h at 1550°C (marker = 20 μm). The dark lines are ridges on the crystal surface shadowed by the evaporated Au/Pd coating. This coating was removed prior to the anneal to prevent possible contamination.

subsequently freeze into the highly irregular flower-like formation seen on the edges, or the relatively regular features seen on polished surfaces. The irregular morphology suggests that the molten material has flowed across the surface from the outside of the feature and accumulated at the centre, where it has subsequently frozen. Similar fluid trails, often fairly linear

as seen in Figs. 3 and 4, have been observed on the polished surface joining separate growth features. Evidence for localized melting and subsequent flow of molten material has also been found on the surface of as-grown single crystals [10]. Such solute trails are believed to act as stress-raising sites, which can induce surface cracking during cooling.

The enhanced localized melting and flow observed on broken edges accounts for the more uniform surface appearance of the annealed powders. The incidence of melting on such uneven surfaces is presumably related to the greater density of nucleation sites provided by localized stress concentrations, and in this respect, crushed powder possesses particularly suitable surfaces. Thus at high temperature each particle is covered by a molten skin which subsequently solidifies to give the round smooth morphology illustrated in Fig. 2b. This possible correlation between feature formation and local stress concentrations may explain the rather surprising absence of similar features on the surface of many as-grown single crystals. Defects grown into the crystal at solidification do not apparently act so readily as nucleation sites for localized melting, but the residual thermal stresses existing in the crystal after cooling to room temperature may produce activation sites for localized melting on subsequent annealing. The dependence of the reaction on the surface condition and crystal orientation of YAP single crystal slices, the highly localized nature of the initial growth features and their tendency to assume a crystallographic surface arrangement also suggest that the reaction is related to the underlying defect structure. In particular, the decomposition behaviour could be associated with the formation of defects which act as optical scattering centres in the as-grown single crystals and impair their device performance.

The most surprising aspect of this localized melting model is that it implies a dramatic drop in the melting point. Growth features on polished slices have been observed after an anneal at 1400°C, but in powder form the decomposition begins at 1300°C [7]. YAP has the lowest melting point, 1870°C, of the three reported compounds in the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ system. The present X-ray diffraction study has shown that the skin consists of YAG and the unknown phase X; the melting point of YAG is 1970°C and that of X unknown. These diffraction studies have failed to identify X but have indicated that

TABLE IV Observed melting points of the three established compounds in the $Y_2O_3-Al_2O_3$ system

Work	Observed melting point ($^{\circ}C$)		
	YAG	YAP	YAM
Yoder and Keith [2]	2110 \pm 70 (s.s. reaction 1970)	—	—
Warsaw and Roy [5]	1970	—	2030
Olds and Otto [12]	1970	—	2050
Toropov <i>et al</i> [4]	1930 \pm 20	1875	2020 \pm 20
Mizuno and Noyuchi [6]	1930 \pm 20	1875	2020 \pm 20
Present material	1970 \pm 10	1870 \pm 10	1930 \pm 10

its composition does not lie on the $Y_2O_3-Al_2O_3$ pseudo-binary join. Thus, a possible explanation of the occurrence of this localized melting is the existence of a eutectic involving YAG and X lying close to the pseudo-binary containing YAG and YAP. A significant loss of one of the constituents, most probably oxygen, would shift the composition off the pseudo-binary join into this eutectic region with a consequent drop in melting point. The eutectic temperature would not be greater than $1300^{\circ}C$ (the lowest temperature at which decomposition has been observed) but whether the composition of the surface layer reaches the eutectic composition would depend on the actual oxygen loss.

A continuing constituent loss over a period of time would produce more molten material as observed on the polished slices. However, in the case of a powder, once the skin has formed on each particle, the rate of decomposition drops markedly, since none of the underlying YAP is exposed and very little oxygen loss can occur; a form of liquid encapsulation has taken place. This explains why no further decomposition occurs upon annealing in a reducing atmosphere. Only room temperature grinding, which breaks up the skin exposing the original YAP structure, leads to further decomposition on re-annealing. Remelting a decomposed YAP powder in an oxidizing atmosphere causes reversion to the original YAP structure, implying that the melt absorbs oxygen, thus bringing the composition back to that of YAP. A constituent loss has yet to be confirmed, but if oxygen is lost, then X is likely to be based on one of the intermetallics in the Y-Al system.

The present work shows that the general features of the equilibrium phase diagram for the $Y_2O_3-Al_2O_3$ pseudo-binary system are essentially correct, containing one stable intermediate compound, YAG, and two metastable phases,

namely YAP and YAM. The deviations in behaviour observed in the present work can be accounted for by oxygen loss.

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References

1. B. COCKAYNE, "Modern Oxide Materials" (Academic Press, London, 1972).
2. H. S. YODER and M. S. KEITH, *Amer. Mineral.* **36** (1951) 519.
3. S. GELLER and E. A. WOOD, *Acta Cryst.* **9** (1956) 563.
4. N. A. TOROPOV, I. A. BONDAR, F. YA. GALADHOV, KH. S. NIKOGOSYAN and N. V. VINOGRADOVA, *Izv. Akad. Nauk. SSSR, Ser. Khim.* **7** (1969) 1158.
5. I. WARSHAW and R. ROY, *J. Amer. Ceram. Soc.* **42** (1959) 434.
6. M. MIZUNO and T. NOGUCHI, *Rep. Gov. Ind. Res. Inst. of Nagoya* **16** (1967) 171.
7. J. S. ABELL, I. R. HARRIS and B. COCKAYNE, *J. Mater. Sci.* **7** (1972) 1088.
8. W. CLASS, *J. Crystal Growth* **3, 4** (1968) 241.
9. M. J. WEBER, M. BASS, K. ANDRINGA, R. R. MONCHAMP and E. COMPERCHIO, *Appl. Phys. Letts.* **15** (1969) 342.
10. B. COCKAYNE, B. LENT, J. S. ABELL and I. R. HARRIS, *J. Mater. Sci.* **8** (1973) 871.
11. B. COCKAYNE and J. G. PLANT, unpublished work.
12. L. E. OLDS and H. E. OTTO, "Phase Diagrams for Ceramists" (edited by E. M. Levin *et al*) (Amer. Ceram. Soc., Columbus, Ohio, 1969) Fig. 311.
13. J. S. ABELL, I. R. HARRIS and B. COCKAYNE, *J. Mater. Sci.* **8** (1973) 667.
14. S. J. SCHNEIDER, R. S. ROTH and J. S. WARING, *J. Res. Nat. Bur. Stand.* **65A** (1961) 345.

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