JOURNAL OF MATERIALS SCIENCE 29 (1994) 4686–4693

Formation of barium–tantalum oxynitrides

A. HELLWIG, A. HENDRY
Department of Metallurgy and Engineering Materials, University of Strathclyde, Glasgow, UK

Oxynitride powders suitable for sintering to form dielectric ABO_3-type perovskites have been prepared by nitriding barium carbonate and tantalum oxide. Both heat treatment in air and reaction in flowing ammonia yield isostructural oxynitride phases, but the amount and electronic state of the oxynitrides depend on the nitriding gas conditions. A red-brown oxynitride of high nitrogen content is described as $Ba_2Ta_2O_3N_2$ containing Ta(IV) ions, but after heat treatment in air the colour changes to white indicative of Ta(V) and a stoichiometry of $BaTaO_2N$ results. A third possibility is identified in an oxynitride containing both Ta(IV) and Ta(V) with an intermediate nitrogen content. Through studies involving thermal analysis and X-ray diffraction, the materials are characterized in powder form and possible sintering conditions are suggested which involve a rapid heating rate and a densification temperature of 1500 °C.

1. Introduction

The dielectric layer of conventional multilayer capacitors consists of type ABO_3 perovskites, and cost-effective capacitor production requires *in situ* sintering of the dielectric layers stacked between the metal electrodes. An oxide dielectric is sintered under an oxygen partial pressure sufficient to prevent reduction of the oxide and because most electrodes oxidize at high temperatures, precious metals of the palladium group have to be used for the metal contacts. The development of novel dielectrics aims at broadening the choice of suitable electrodes and hence a reduction of the production cost and one alternative would be dielectric materials which can be sintered in a reducing atmosphere, e.g. nitrogen. Retaining the well-known perovskite structure, Marchand *et al.* [1] altered the character of the dielectric by replacing a part of the oxygen by nitrogen. The product was a cubic oxynitride phase $BaTaO_2N$ with promising dielectric properties. To ensure a reproducible dielectric constant of the interlayer the phase composition, impurity content and microstructure (porosity and grain size) of polycrystalline dielectrics have to be closely controlled [2]. The first of these is the object of the present study of the phase composition of Ba–Ta oxynitride material.

Ba–Ta oxynitride powder is produced by thermal treatment of oxide powder in an ammonia atmosphere (ammonia is a suitable source of high nitrogen partial pressure as discussed below). A preliminary investigation [3] proved that formation and decomposition of the desired oxynitride phase are strongly dependent on process conditions such as temperature and nitrogen potential. The production of the dielectric can be divided into two steps: after nitridation of the oxidic precursor material, sintering of the powder is necessary to form a dense material. The temperature and nitrogen potential of sintering are different from those applied in nitridation, which jeopardizes the stability of the oxynitride compound. In this work the formation mechanism and the stability of the oxynitride perovskite is investigated under different oxygen and nitrogen partial pressures at high temperatures. Powder samples were examined by X-ray diffraction (XRD) analysis to identify phase transformations and simultaneous thermal analysis (STA) was used to understand decomposition and predict sintering behaviour.

2. Experimental procedure

All powders were prepared from 99.0% $BaCO_3$ powder (Analar) and 99.0% Ta_2O_5 powder (Aldrich). The powder was mixed in a ratio of 2 mol $BaCO_3$ to 1 mol Ta_2O_5. It was blended in a ball mill in a solution of propan-2-ol for at least 6 h and then the solution was dried under a radiant heater until the solvent had evaporated. Nitridation was carried out under commercial NH_3 gas in a horizontal tube furnace, except for batches C, D and E which were prepared in a vertical furnace. The heating rate was about 15 °C min^{-1} for both furnaces, determined by the velocity with which the boat was pushed into the hot zone. An ammonia gas stream was maintained for periods between 2 h and 26 h at a temperature of 800 or 1000 °C. One experiment was carried out under air to cross-check the results. The flow rate determines the length of time spent by each NH_3 molecule in the hot zone of the furnace and is therefore correlated with the nitrogen fugacity. Flow rates were varied between 150 and 900 $cm^3\ min^{-1}$, but a flow rate of 350 $cm^3\ min^{-1}$ was commonly used for the horizontal furnace.

After nitridation the homogeneity of the product was analysed. In a long alumina boat the colour of the powder near to the gas inlet differed significantly from that of the powder at the opposite end of the boat. In order to separate powders of different colours the batch was divided into three to seven batches, accounting for the position in the boat. In order to achieve a more homogeneous nitridation the direction of the gas stream in experiments H, J and K was reversed for about half the heat treatment time. Powder L was made of selected parts of previously prepared batches (F, G, H, J, K), which were mixed together (in a ball mill in propan-2-ol solution) and nitrided a second time for 26 h, with a reversing gas stream.

XRD analysis was carried out on powdered material (after crushing in a mortar), mixed with a small amount of vaseline. A two-circle goniometer was used for the analyses (CoK_α radiation, 40 kV, 20 mA). Thermal analysis was carried out in PL–Thermal Sciences STA-1600 and TMA-1400 equipment on powders and solid compacts, respectively. Heating and cooling rates in the simultaneous thermal analysis (STA, differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were $20\,^\circ\mathrm{C\,min}^{-1}$. A rate of $30\,^\circ\mathrm{C\,min}^{-1}$ was applied in the dilatometer analysis. X-ray photoelectron spectroscopy (XPS) analysis was carried out on powder samples using AlK_α radiation generated at 10 kV and 20 A in a VG Scientific instrument. The observed binding energies had to be corrected to take account of a shift due to charging of the material. The correction was made with respect to the carbon C1s peak, which should be at 284.6 eV. The accuracy of the observed energies is ± 0.1 eV.

3. Results and discussion

3.1. Formation of oxynitrides in NH_3 and air

3.1.1. *Discussion of NH_3 nitriding*

The overall decomposition of ammonia can be summarized as follows:

$$NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$$

gives the overall statement of the decomposition equilibrium, and since the free energy for the reaction is well known, it is possible to calculate the equilibrium constant $K(T)$ and hence the nitrogen potential if the degree of dissociation of the gas is known (for example, by exit gas analysis from the furnace):

$$\log K(T) = \log[(p_{N_2})^{1/2}(p_{H_2})^{3/2}(p_{NH_3})^{-1}]$$

or

$$\log p_{N_2} = 2\log K(T) + 2\log p_{NH_3} - 3\log p_{H_2}$$

It must be recognized, however, that this is the nitrogen potential or fugacity associated with the ammonia molecules and is not the potential (or pressure) of the diatomic nitrogen molecules arising as the products of decomposition. These N_2 molecules are no more effective in nitriding the ceramic than N_2 gas added from a gas cylinder.

The mechanism by which this nitriding potential is released on the surface of the powder is an altogether more complex matter. The surface of the ceramic may be considered to have a finite number of sites available for adsorption of gas species, and the proportions of these are assumed to be those in the gas phase immediately above the surface. The gas is itself maintained at an equilibrium state by the flowing gas stream. From the results below it will be seen that this latter aspect is not the case in the present experiments, although this does not negate the general discussion of nitriding mechanisms. The ceramic surface therefore has adsorbed nitrogen, hydrogen and ammonia molecules. The relative concentration of ammonia is small relative to nitrogen and hydrogen as shown by the exit gas analysis, but the chemical potential for nitriding is very high. The surface decomposition reactions are not completely characterized but are suggested to adopt the following mechanism by analogy with the nitridation of metals:

$$2NH_3(ads) \rightarrow 2NH_2(ads) + H_2$$

where H_2 is the combination of two atoms of hydrogen released (on the surface) by the ammonia molecules and desorbed into the gas. This is followed by two similar steps,

$$2NH_2(ads) \rightarrow 2NH(ads) + H_2$$

$$2NH(ads) \rightarrow 2N(ads) + H_2$$

which give atomic (active) nitrogen on the surface at the high fugacity given by the equation above for p_{N_2}. In order to nitride the underlying ceramic, exchange then occurs between the oxide anions in the surface and the adsorbed nitrogens to give nitride anions, and the oxygen is removed into the gas by reaction with the high concentration of surface hydrogen to form water vapour molecules. As a result of the different anionic charges of the nitride and oxide anions there will therefore be a corresponding change of valence state of the host cations, which as shown below primarily involves the tantalum cations.

These processes involve nitridation at extremely high equivalent nitrogen potentials. For example, at 900 °C in pure ammonia inlet gas with 1% NH_3 in the exit gas, the equation for p_{N_2} given above becomes

$$\log p_{N_2} = 2\log(4644) + 2\log(0.005) - 3\log(0.746)$$

i.e.

$$p_{N_2} = 1.3 \times 10^3 \text{ atm}$$

Thus it can be understood that on removal of the nitriding gas atmosphere and heating in any other gas there will be a strong tendency for decomposition of the oxynitride to a lower nitrogen (higher oxygen) content.

Tables I and II show the results of nitriding experiments under different experimental conditions. The rate of nitrogen pick-up is significantly higher at 1000 °C compared to 800 °C, and at 1000 °C the nitrogen pick-up obeys a first-order reaction rate with respect to time. The colour of the powder depends likewise on the nitridation parameters. The change from red-brown colour to the lighter colours correlates with a decrease in N content. The observed colours are partly mixed colours and can be derived from three basic colours, white, yellow and red-brown. These states reflect three different electronic states of the material.

TABLE I Experimental conditions for nitriding experiments

Batch	Temperature (°C)	Time (h)	Flow rate (cm^3 min^{-1})	Colour(s), with respect to position of the powder in the reaction boat
A1	1000	16	150	Red/brown
A2	1000	6	150	Brown
A3	1000	4	150	Orange
A4	1000	2	150	Yellow/brown
A5	1000	11	150	Orange/red
A6	800	6	150	Orange/light brown
A7	800	4	150	Grey/light brown
A8	800	2	150	Yellow/green
B1–B7	1000	10	150	Green/brown-grey
C1–C5	1000	15	150	Brown-grey
D1–D4	1000	16	700	Brown-grey
E1–E3	1000	16	900	
F1–F3	1000	16	350	Brown-yellow
G1–G3	1000	17	350	Brown-green/brown
H1–H4	1000	20 (rev)[a]	350	Light brown-brown
J1–J4	1000	23 (rev)	350	Light brown-brown
K1–K4	1000	20 (rev)	350	Light brown-brown
L (pre-treated powder)	1000	26 (rev)	350	Brown
O (treated in air)	1000	18	0	White

[a](rev) = direction of gas flow reversed twice during nitridation.

TABLE II Colour, nitrogen content and XRD analysis after nitridation

Batch	Colour	N (wt%)	Observed phases	I^p/I^h	Remarks
A8	Yellow/green	0.5	Cubic O–N + $Ba_5Ta_4O_{15}$	0.58	–
A6	Orange/light brown	0.7	Cubic O–N + $Ba_5Ta_4O_{15}$	0.79	–
A3	Orange	2.0	Cubic O–N + $Ba_5Ta_4O_{15}$ + $BaTa_2O_6$	0.85	–
A5	Orange/red	2.5	Cubic O–N + $Ba_5Ta_4O_{15}$	1.8	–
A1	Red/brown	3.3	Cubic O–N + $Ba_5Ta_4O_{15}$	4.25	–
D1 (at gas inlet)	Red/brown	2.6	Cubic O–N + $Ba_5Ta_4O_{15}$ + $BaTa_2O_6$	5.3	–
D4 (at gas outlet)	White/grey	0.3	Cubic O–N + $Ba_5Ta_4O_{15}$	0.56	Weak extra peak of 9-L-perovskite
F1 (at gas inlet)	Brown	1.9	Cubic O–N + $Ba_5Ta_4O_{15}$	1.8	–
F3 (at gas outlet)	Yellow/brown	0.4	Cubic O–N + $Ba_5Ta_4O_{15}$ + $BaTa_2O_6$	0.56	–
J3 (centre of furnace)	Brown	1.3	Cubic O–N + $Ba_5Ta_4O_{15}$ + $BaTa_2O_6$	0.87	–
O	White	0.01	Cubic O–N + $Ba_5Ta_4O_{15}$ + $BaTa_2O_6$	0.6	Weak extra peak of 9-L-perovskite
L	Red/brown	–	Cubic O–N + $Ba_5Ta_4O_{15}$ + $BaTa_2O_6$	2	–

Samples taken from opposite ends of the nitriding container reveal that the nitrogen content of the powder is higher the nearer the powder is located to the gas inlet (e.g. D1 and D4, F1 and F3). The reason for this inhomogeneity is the nitrogen fugacity, which varies along the length of the furnace. Temperature and the decomposition constant of ammonia are constant in the hot zone of the furnace, but another factor determining the fugacity is the dissociation degree of ammonia, α. As ammonia streams continuously into the hot furnace, α increases with increasing distance from the gas inlet, and the resulting fugacity reaches a maximum at the gas inlet side of the hot zone and decreases sharply after passing this point. Reversing the gas stream during nitridation helps to counterbalance the differences in N content. An increase in the fugacity is accomplished by raising the flow rate of NH_3, as seen from comparison of batches D1 and F1 in Table II. A full discussion of this behaviour is given by Elphinstone and Hendry [3].

The observed differences in nitrogen content reflect different amounts of oxynitride phase and/or different oxygen to nitrogen ratios in the existing phases. It is known from previous examinations [1] that one particular oxynitride phase with a proposed oxygen/nitrogen ratio of 2:1 has a characteristic dark red-brownish colour. This phase has the perovskite structure shown in Fig. 1, and is given as $BaTaO_2N$ by Marchand *et al.* [1] who used neutron diffraction experiments to prove that oxygen and nitrogen atoms are distributed statistically on the face-centred lattice sites (3c). It has to be noted that small deviations from the proposed ratio of two oxygen to one nitrogen atom would also be in accordance with the reported results.

In this investigation it was found that different process conditions yield the formation of phases which are closely related to the previously described oxynitride. A literature survey reveals that data about Ba–Ta oxynitrides are rare, but among the perovskite

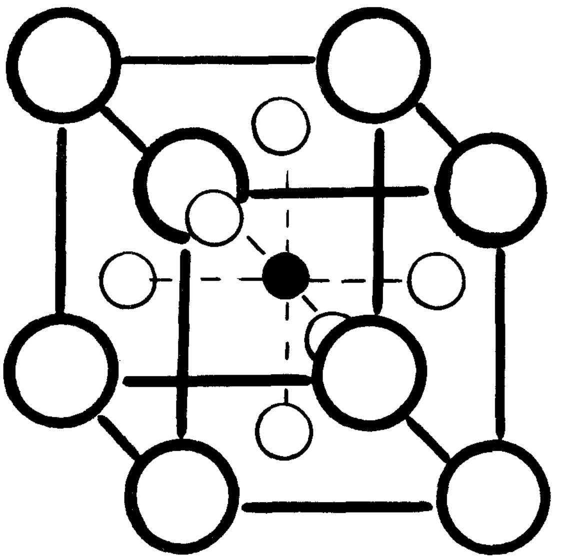

Figure 1 Perovskite structure of $BaTaO_2N$ as proposed by Marchand *et al.* [1]: large circles = Ba atoms, small circles = O/N atoms, filled circle = Ta atom.

structures there are several Ba–Ta phases reported which have a similar composition of Ba/Ta/O, but no nitrogen. These different types of perovskite vary mainly in the stacking sequence of the common unit cell. Table III shows a summary of observed barium tantalates with structures based on the perovskite structure, according to Kemmler-Sack [4].

3.1.2. Identification of coexisting phases

The results of XRD analyses are given in Table II. All nitrided powders comprised a phase with the cubic perovskite structure ($a = 0.410$ nm), as described by Marchand *et al.* [1], plus a hexagonal phase identified as $Ba_5Ta_4O_{15}$ [6] (see Table III). Even the prolonged heat treatment of batch L did not yield complete transformation to single-phase oxynitride. The lattice parameter a of the phase $Ba_5Ta_4O_{15}$ differs significantly from the value reported in the literature (this study: $a = 0.501$ nm, $c = 0.119$ nm; literature value: $a = 0.579$ mm [7]). A reason for this may be minimization of the lattice mismatch with the coexisting cubic perovskite phase. The observed a axis of 0.501 nm matches the lattice parameter of the cubic phase (0.409 nm), if multiplied by a factor of $2^{1/2}/3^{1/2}$. As a consequence several lines of the hexagonal $Ba_5Ta_4O_{15}$ (index h) and the cubic perovskite (index p) coincide: $(110)_h = (111)_p$, $(300)_h = (211)_p$, $(220)_h = (220)_p$.

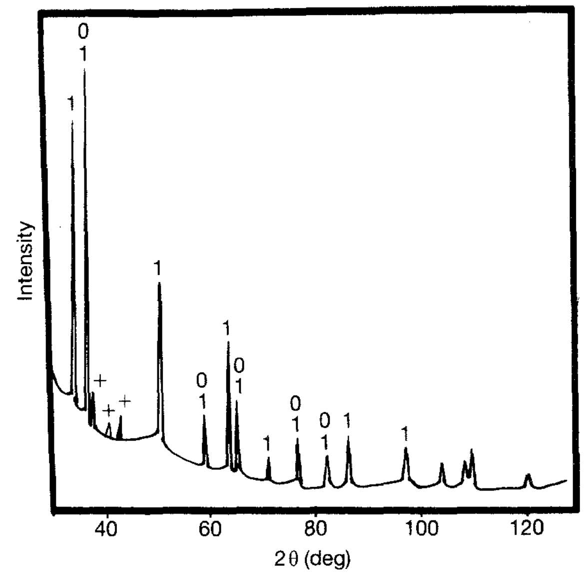

Figure 2 Schematic X-ray diffraction trace of reacted powder: (1) $Ba_5Ta_4O_{15}$, (O) $BaTaO_2N$, (+) $BaTa_2O_6$.

TABLE III Summary of barium tantalates with structures based on the perovskite unit cell (expanded from [4])

Phase (experimental conditions)[a]	Symmetry	Lattice constants (nm)	Structure type, source
$Ba_{12}Ba_{2\,1/3}Ta_{7\,1/3}\,\square_2O_{33}\square_3$ (900 °C)	Rhombohedral	$a = 0.5922$ $c = 9.34$	36L, [4]
$Ba_3BaTa_2O_9$ (1050 °C)	Hexagonal	$a = 0.610$ $c = 0.805$	3L, [5]
$Ba_5BaTa_3\,\square O_{13\,1/2}\square_{1\,1/2}$ ($T > 1050$ °C)	Distorted hexagonal	$a = 0.6075$ $b = 1.058$ $c = 1.610$	6L, [5]
$Ba_5Ta_4O_{15}$ (800 °C, 1100 °C)	Hexagonal	$a = 0.5776$ $c = 1.182$	5L, [6, 7]
$Ba_5Ta_4O_{13}$ (blue) (1150 °C, sealed glass)[b]	Hexagonal	As above	5L, [7]
$Ba_{0.5}TaO_3$ (1100 °C)	Tetragonal	$a = 1.260$ $c = 0.395$	W-bronze, [8]
$Ba_{0.5}TaO_{2.5}$ (blue) (1100 °C, sealed glass)[b]	Tetragonal	As above	W-bronze (conducting), [8]
$Ba_5Ta_{10}O_{30}$	Tetragonal	$a = 1.259$ $c = 2 \times 0.039$	W-bronze (ferroelectric), [9]
$BaTa_2O_6$	Orthorhombic	$a = 1.106$ $b = 0.750$ $c = 0.537$	$CaTa_2O_6$, [10]

[a] Atmosphere: air, unless stated otherwise.

[b] Plus addition of Ta metal as a source of electrons.

Fig. 2 shows a typical XRD diagram, indexed for the cubic perovskite and $Ba_5Ta_4O_{15}$. The amount of the cubic oxynitride phase and hexagonal $Ba_5Ta_4O_{15}$ in different specimens can be ranked by comparing the intensity of the highest peaks of either phase. The ratio I^p/I^h rises with increasing N content of the specimens (compare Table II). Assuming that $Ba_5Ta_4O_{15}$ contains only a negligible amount of N, the cubic phase contains the majority of the incorporated N atoms.

A small percentage of a third phase was observed in most specimens. Repeating the XRD analysis with a longer counting time allowed this phase to be identified as $BaTa_2O_6$ [8]. The two specimens of lowest N content and white colour exhibited an extra peak of low intensity which could not be attributed to any of the previously mentioned phases. It is an indication of a hexagonal superstructure of the cubic perovskite cell, probably with a periodic sequence of nine layers of perovskite cells. This structure is closely related to the five-layered hexagonal perovskite structure of $Ba_5Ta_4O_{15}$.

3.1.3. Isostructural oxynitride phases of different colours

As all the different coloured specimens listed in Table II consist of the same structures in varying amounts, the changes in the electronic structure of the material are obviously not reflected in the crystal lattice. Ba–Ta oxides are known for their ability to change the electronic state without a change in the lattice structure: $Ba_5Ta_4O_{15}$ and $BaTa_2O_6$ can both exist in two states, based on a change of the valency of the Ta ion [7, 8]. $BaCO_3$ and Ta_2O_5 form at high temperatures ($\geq 1100\,°C$) in a reducing atmosphere the oxygen-deficient phases $Ba_5Ta_4O_{13}[\,]_2$ and $BaTa_2O_5[\,]$, with Ta(IV) ions. These phases are isostructural with the phases with Ta(V) ions. Both of the oxygen-deficient phases are of a significant blue colour, whereas the oxygen-sufficient material is white. The oxygen-deficient oxides are not present in significant amounts in the specimens listed in Table I, since no blue colour was observed. Nevertheless it is possible that Ta(IV) ions are incorporated in an oxynitride phase. As the presence of Ta(IV) ions seems to be correlated with intense colours, it is postulated that the phase prevailing in the red-brown powder comprises Ta(IV) ions, in which case its stoichiometrical description as $BaTaO_2N$, as assumed by Marchand *et al.* [1], is no longer appropriate. To account for the high nitrogen content in this phase a new formula of the type $Ba_2Ta_2^{IV}O_3N_2\,[\,]$ is proposed. This formula takes into account the cubic perovskite structure of the phase, which requires a formula of the type $A_xB_x(O, N, [\,])_{3x}$. A Ba/Ta ratio of roughly 1:1 is fixed by the powder mixture used and the O/N ratio is chosen in such a way that the new average Fermi length varies by only 3.4% up from the one suggested by Marchand *et al.* [1].

In analogy with the Ba–Ta oxides a phase of the type $BaTaO_2N$, with Ta in the V^+ state, is of white colour. This is the isostructural phase observed in specimen O. On the basis of this, the yellow colour of specimens with medium N content can be attributed to a third isostructural oxynitride with a formula of the type $Ba_4Ta_2^{IV}Ta_2^{V}O_7N_4\,[\,]$.

The difference in the valency state of the Ta ions was proved by an XPS investigation of the red-brown powder (batch L) and the white powder (batch O). Fig. 3 shows a comparison of the observed Ta peaks. The results derived from the observed Ta peaks are listed in Table IV. The red powder revealed lower binding energies for the $Ta4f_{7/2}$ and $4f_{5/2}$ states than the white powder (shift about 0.5 eV). The lower binding energy can be attributed to a state of higher electron density in the outer shell of the Ta(IV) ion.

The three suggested isostructural phases $Ba_2Ta_2O_3N_2$ (red-brown), $Ba_4Ta_4O_7N_4$ (yellow) and $BaTaO_2N$ (white) contain 3.93, 3.89 and 3.84 wt % N, respectively, according to the formulae. Comparing the calculated with the measured N contents (in Table II), it has to be taken into account that a second (and small amounts of a third) phase was found in all

TABLE IV Results of XPS analyses

Observed peak	Binding energy (eV) in white powder (O)	Binding energy (eV) in red powder (L)
$Ta4f_{7/2}$	25.4	24.82
$Ta4f_{5/2}$	27.2	26.72
Delta-4f	1.8	1.9

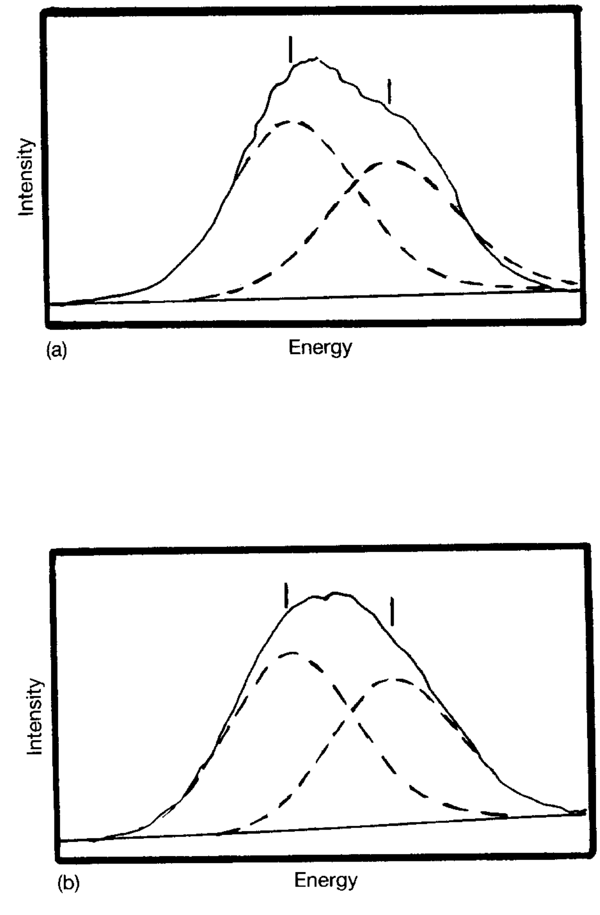

Figure 3 Schematic X-ray photoelectron spectroscopy traces of the Ta4f peaks (the values of energy and energy shift are given in Table IV) : (a) red powder, (b) white powder.

specimens (Table II). Some further adjustment of the proposed formulae may be necessary, but in this study the formulae were kept to simple stoichiometries.

3.1.4. Reaction mechanisms

The following reaction mechanisms can thus be postulated. There are two preliminary reaction steps:

I: $BaCO_3 \rightarrow BaO + CO_2$ (enhanced by the presence of NH_3)

II: $6BaO + 3Ta_2O_5 \rightarrow Ba_5Ta_4O_{15} + BaTa_2O_6$

According to the partial pressures of O and N, Reactions III or IV then V will follow:

III: $2Ba_5Ta_4O_{15} + 2BaTa_2O_6 + 6N_2$
$\rightarrow 12BaTaO_2N + 9O_2$

or under high N partial pressures

IV: $2Ba_5Ta_4O_{15} + 2BaTa_2O_6 + 6N_2$
$\rightarrow 3Ba_4Ta_4O_7N_4 + 10\frac{1}{2}O_2$

followed by Reaction V after Reaction IV is completed:

V: $Ba_4Ta_4O_7N_4 \rightarrow 2Ba_2Ta_2O_3N_2 + \frac{1}{2}O_2$

If the gas atmosphere does not allow a complete transformation into $Ba_2Ta_2O_3N_2$, the reaction product will be a mixture of $Ba_2Ta_2O_3N_2$ (red) and

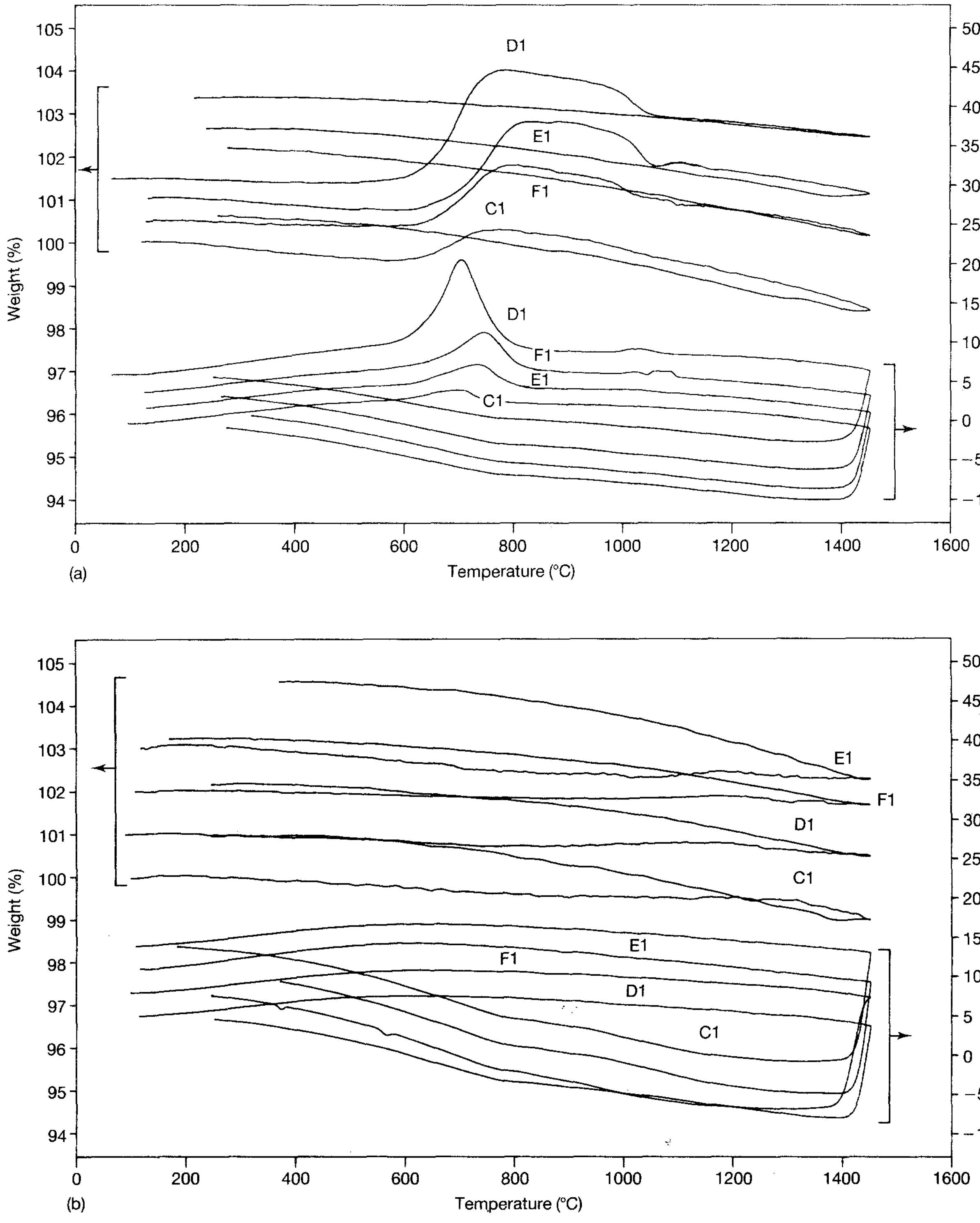

Figure 4 DTA and TGA traces of specimens C1–F1 in (a) air atmosphere, (b) nitrogen.

$Ba_4Ta_4O_7N_4$ (yellow), and the colour of the material is the related colour mixture (orange).

3.2. Decomposition of oxynitride phases in different atmospheres

The stability of $Ba_2Ta_2O_3N_2$ in air or nitrogen was tested in STA experiments in order to find appropriate sintering conditions for the oxynitride powder. Fig. 4 shows the DTA and TGA traces for four different specimens heated in flowing air up to 1450 °C. In the course of the heating all specimens reveal an exothermic reaction combined with weight gain, and a much less significant reaction at higher temperature, linked with a slight weight loss. While cooling down the TGA trace does not show any changes in slope and the DTA curve exhibits no more peaks, indicating that none of the two reactions is reversible.

In all specimens an exothermic reaction starts at about 650 °C and a second reaction begins at 1000 °C. The intensity of both reactions, in terms of heat and weight change, depends on the nitrogen content of the sample. The specimen with the highest initial N content (D1) exhibits the largest exothermic and endothermic peaks. The weight gain after the complete DTA run proved to be likewise related to the N content.

Following from the curves in Fig. 4a, additional samples of powder D1 were exposed briefly to temperatures of 590, 850 and 1100 °C (in air). Colour and XRD analysis after this heat treatment allow the phase transformations to be assigned to the DTA peaks. After being heated up to 590 °C the sample had the same colour as the as-nitrided D1, indicating that Ta(IV) ions were still present. The X-ray diagram confirmed that no phase transformation had occurred. After heat treatment in air for 2 h at 850 °C the colour of the material had changed completely to white, and an interrupted DTA run up to 900 °C (with a heating rate of 20 °C min^{-1}) showed the same colour change even after this short heat treatment. The exothermic reaction involves a change in valency from Ta(IV) to Ta(V) and XRD shows furthermore an increase in the amount of the phases $Ba_5Ta_4O_{15}$ and $BaTa_2O_6$. It is concluded from these observations that the input material oxidizes at 650 °C, combined with a weight gain. The proposed reaction is

$$4Ba_2Ta_2O_3N_2 + \frac{13}{2}O_2 \rightarrow 2BaTaO_2N + Ba_5Ta_4O_{15} + BaTa_2O_6 + 3N_2$$

All the reaction products are of white colour. For a starting material consisting only of $Ba_2Ta_2O_3N_2$, the weight gain caused by this reaction would have been 4.35%. Since the as-nitrided powder D1 contained a noticeable amount of $Ba_5Ta_4O_{15}$ as a second phase, the observed weight gain is only 2.6%.

The same specimen heat-treated in air up to 1100 or 1450 °C did not show any further change in colour, nor a further noticeable change in the phase composition as determined by XRD. The second reaction at 1000 °C is thus not a structural transformation of Ba–Ta oxynitride, $Ba_5Ta_4O_{15}$ or $BaTa_2O_6$. Neither is an oxidation concerned, because the weight decreases. For this second reaction it has to be considered that the phases, which were established during nitridation and not involved in the previous oxidation, might become unstable as soon as 1000 °C is exceeded. The only possible phase transformation, causing a weight loss under an oxygen partial pressure, is the reaction of $BaCO_3$ to BaO arising from small amounts of carbonate unconverted in the original powder.

To check this presumption pure $BaCO_3$ was exposed to the same DTA conditions as specimen D1. $BaCO_3$ revealed two structural transformations at 820 and 973 °C (without weight change) and a weight loss of about 21%, setting in at about 1050 °C. This reaction is combined with an endothermic peak. The theoretical weight loss for the reaction $BaCO_3 \rightarrow BaO + CO_2$ is 22.3%. It was calculated that a small amount of residual $BaCO_3$ in the as-nitrided material – only 1.6% – is sufficient to result in an overall weight loss of 0.7% (as observed in D1). The weight change combined with the transformation of $BaCO_3$ is larger in specimens of high N content and a small amount of $Ba_5Ta_4O_{15}$. They contain probably a higher proportion of residual $BaCO_3$ in the as-nitrided state. On the other hand the formation of a large amount of $Ba_5Ta_4O_{15}$ is correlated with enhanced "consumption" of $BaCO_3$ during nitridation. This result is consistent with an observation made by Galasso and Katz [7] in which it was remarked that the best way to prepare the phase $Ba_5Ta_4O_{15}$ from $BaCO_3$ and Ta_2O_5 is by adding about 2% $BaCO_3$ in excess of the stoichiometrically calculated amount.

3.2.1. Decomposition in N_2

The DTA traces of nitrided powders heated in N_2 do not show any effects as significant as those seen in the examination in air. They all have a gradual change in the slope of the trace and the slope of the TGA curve does not change significantly throughout the whole cycle. An overall weight gain of 1.5% is observed in specimens of high starting N content. The weight gain in specimens of lower N content is less (in specimen A8 no weight change is observed at all). No colour change is observed after heating specimen A1 up to 700 °C, but after exposure to 1100 °C the colour of the specimen changed to white. The phase changes identified by XRD are very similar to the ones observed in DTA runs in air: the amounts of $Ba_5Ta_4O_{15}$ and $BaTa_2O_6$ increased at the expense of the cubic perovskite phase, but the phase composition did not change as much as in air.

The phase transformation between 700 and 1100 °C in N_2 is believed to be decomposition of $Ba_2Ta_2O_3N_2$ into $BaTaO_2N$, $Ba_5Ta_4O_{15}$ and $BaTa_2O_6$ and the oxygen required for this transformation is probably provided by reduction of $Ba_5Ta_4O_{15}$ or $BaTa_2O_6$. However, it is not clear why the reaction product does not reveal the blue tinge typical of the oxygen-deficient tantalates. The reaction sets in at slightly higher temperatures in N_2 (above 700 °C) compared to the oxidation in air (650 °C), and is considerably slower. The melting temperature of the material (specimen A8) was determined in a DTA cycle up to 1650 °C under N_2, where a strong endothermic peak was observed at 1570 °C.

These results show that effective sintering of the oxynitride phase will be possible in nitrogen provided that a sufficiently rapid heating rate is used up to about 1500 °C. Rapid heating will result in closure of open porosity before significant decomposition of the oxynitride will occur and thereafter final (slower) pore elimination will proceed in equilibrium with the solid phase.

4. Conclusions

Ba–Ta oxynitrides of cubic perovskite structure were prepared by nitriding a mixture of $BaCO_3$ and Ta_2O_5 under different experimental conditions. Heat treatment in air and nitridation under flowing NH_3 yielded isostructural oxynitride phases, but the amount and electronic state of the oxynitride depended strongly on the nitrogen fugacity. The red-brown coloured oxynitride of high nitrogen content contains Ta ions in the reduced IV^+ state, and is therefore not correctly described by the formula $BaTaO_2N$. A stoichiometrical composition of $Ba_2Ta_2O_3N_2$ is postulated instead. After heat treatment in air an oxynitride of white colour is observed, indicating the presence of Ta(V) ions. The formula $BaTaO_2N$ was attributed to this phase. A third possibility for forming the perovskite structure is by incorporating Ta(IV) as well as Ta(V) ions. It is assumed that this state exists in the powder of yellow colour with an intermediate N content.

The decomposition of the oxynitride $Ba_2Ta_2O_3N_2$ in air and nitrogen was investigated by STA combined with XRD analyses. $Ba_2Ta_2O_3N_2$ oxidizes in air at 650 °C to form $BaTaO_2N$ and Ba–Ta oxides. A similar effect is observed while heating in N_2, but the transformation is much slower. A potential method for preservation of the $Ba_2Ta_2O_3N_2$ phase during consolidation is envisaged for sintering in nitrogen, on condition that the material is heated rapidly and sintered at a temperature close to 1500 °C.

References

1. R. MARCHAND, F. PORS, Y. LAURENT, O. REGRENY, J. LOSTEC and J. M. HAUSONNE, *J. Physique* **47** (1986) Colloque C1, Suppl. No. 2, p. 901.
2. N. W. THOMAS, *Met. Mater.* **7** (1991) 741.
3. I. ELPHINSTONE and A. HENDRY, in Proceedings 45, "Fabrication Technology" (Institute of Ceramics, Stoke on Trent, UK, 1989) p. 15.
4. S. KEMMLER-SACK, *Z. anorg. allg. Chemie* **476** (1981) 109.
5. *Idem, ibid.* **471** (1980) 109.
6. J. SHANNON and L. KATZ, *Acta Crystallogr.* **B26** (1970) 102.
7. F. GALASSO and L. KATZ, *ibid.* **14** (1961) 647.
8. F. GALASSO, L. KATZ and R. WARD, *J. Amer. Chem. Soc.* **81** (1959) 5898.
9. I. G. ISMAILZADE, *Kristallografiya* **5** (1960) 268.
10. Y. REPELIN, E. HUSSON, NGUYEN QUY DAO and H. BRUSSET, *Mater. Res. Bull.* **15** (1980) 985.
11. I. ELPHINSTONE, PhD thesis, University of Strathclyde, Glasgow (1992).

Received 18 January
and accepted 21 March 1994