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Preparation and properties of pigmentary grade $BiVO_4$ precipitated from aqueous solution

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Abstract

Bismuth vanadate, nominally $BiVO_4$, is used as a yellow pigment in the ceramic and plastic industries. It can be prepared by heating stoichiometric quantities of Bi and V precursors but brighter colours are obtained by an aqueous preparation route. Depending on precipitation conditions, either a zircon- or scheelite-structured phase may be obtained. Thermal analysis, coupled with effluent gas analysis and X-ray diffraction of the heated zircon-structured solid, discloses complex phase transitions in the range 200–450 °C. Initially the zircon-structured phase transforms to a scheelite-structured phase which, on cooling, converts to a fergusonite-structured phase. The crystallographic changes during the heating cycle are accompanied by a two-stage weight loss, totalling ~2.0–3.0 wt.%: evolved gas species are principally nitrogen oxides and water. The structural role of these volatiles is examined. The pigmentary colour achieved depends, in part, on the microstructure, stoichiometry and density of the precipitated product as well as the sequence of phase transformations with loss of volatiles, all of which influence the complex texture and defect structures of the calcined product.

Keywords: A. Powders: chemical preparation; C. Colour; $BiVO_4$; Pigments

1. Introduction

Bismuth vanadate, nominally $BiVO_4$, is widely used as a ceramic pigment associated with yellow colours. As such, it is often used as a replacement for cadmium-based yellows. $BiVO_4$ may be made by a ceramic route: stoichiometric quantities of Bi- and V-containing precursors are mechanically mixed and heated to ~700 °C in air or other oxidising atmosphere. However, colours produced from ceramic preparations are often dull. On that account, a two stage process is often used involving as the first step, precipitation of $BiVO_4$ from acidic mixed solutions containing Bi(III) and V(V). The resulting powder is recovered and dried and may be calcined in a second step. In any event it will be calcined in the course of ceramic applications and may undergo moderate heating in the course of forming pigmented thermoplastics [1–8].

Bismuth vanadate is polymorphous, as shown in Fig. 1. Three polymorphs are known having the zircon, scheelite and fergusonite structure types. All three crystal structures are well established and are characterised by having tetrahedral V, which is co-ordinated by four oxygens, with Bi having eightfold co-ordination: its co-ordination sphere can be envisaged as consisting of two interpenetrating tetrahedral of unequal size [9,10]. The zircon-structured phase is a framework type which becomes progressively distorted to more layer-like structures in scheelite and fergusonite. Much attention has been devoted to the mechanism of phase transformations because of the electrical and magnetic properties of the phases: for example, the fergusonite $\rightleftharpoons$ scheelite phase transformation is ferroelastic [11–14]. Phase equilibria studies of the Bi_2O_3–V_2O_5 system disclose that scheelite is the stable high temperature phase; at or below 255 °C it transforms to the fergusonite-structured phase with corresponding reduction in symmetry from $I4_1/a$ to $I2/a$ [15–17]. The reduction in symmetry arises mechanistically because of the need, especially at lower temperatures, to accommodate the lone pair of electrons associated with Bi(III).

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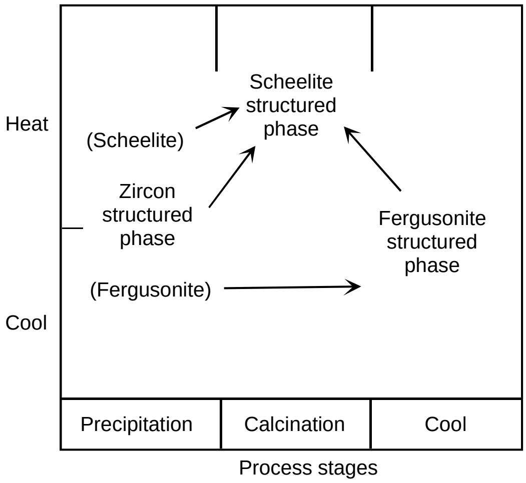

Fig. 1. Scheme of phase transformation of $BiVO_4$ made by precipitation products.

The aqueous preparation route for $BiVO_4$ thus has several novel features. The first is the ready occurrence of a zircon-structured phase for the $BiVO_4$ composition, which is probably metastable. The second novel feature is the occurrence of a nominally anhydrous phase as the product of precipitation from aqueous solution at low (0–100 °C) temperature. The third novel feature is that the zircon-structured phase is not the only product which can be obtained: by adjusting pH, concentration and ageing time, high yields of the scheelite-structured phase can be obtained, also within the temperature range 0–100 °C.

Since colour and colour intensity depend on many factors including phase composition, stoichiometry, particle size and morphology, it has proven difficult to control the pigmentary colours of $BiVO_4$. An investigation was begun on the relationship between colour, preparative conditions and thermal history. This paper reports characterisation data for heated products using as a precursor the zircon-structured phase.

2. Preparation and characterisation

2.1. Preparation

The patent literature discloses specific examples of the preparation of zircon-structured $BiVO_4$ but general literature is sparse [11,18–20]. Some 100 preparations were attempted in the course of the title study. It was necessary to use as precursors acidic aqueous solutions of the reactants to (i) achieve sufficient solubilities of Bi and V, which precipitate as neutrality is approached and (ii) achieve aqueous speciations for both Bi and V which enable them to be coprecipitated as $BiVO_4$; complex cationic and anionic speciations, e.g., polyvanadates, are best avoided as yields of $BiVO_4$ decrease in the presence of stable polyanionic complexes. In general, pH values close to 2 give V(V) mainly speciated as vanadyl (VO_2^+) ions but are insufficiently acid to solubilise bismuth: it is necessary to use still lower pH to achieve Bi solubility and simple speciations. A robust preparative route is as follows: using analytical grade 4 M nitric acid solution as the solvent, dissolve into one beaker the precursor vanadium salt and into another, the bismuth salt. Ammonium metavanadate, NH_4VO_3, is a satisfactory source of V. Good Bi sources are the basic nitrate, $[Bi_6O_4(OH)_4](OH)(NO_3)_5 \cdot 0.5H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$ or $BiONO_3 \cdot H_2O$. All formulae are approximate; the respective stock solutions must be analysed prior to use if exact mixture stoichiometry is deemed to be crucial. These V and Bi stocks solutions, up to ∼0.15 M with respect to either Bi or V, can be kept and when required, mixed in appropriate amounts without precipitation. Precipitation is induced by titration with 30% NaOH solution, continuously stirring the batch and monitoring pH to a predetermined cut-off point. Rate of addition of NaOH affects product properties; slow rates of addition are best achieved using a peristaltic pump for delivery such that pH is increased to ∼1 over minutes or hours. Table 1 shows a range of preparative conditions and the nature of the products obtained. Preparations shown in the table were done at ∼22 °C; other temperatures between 0 and 40 °C gave similar results: “Rapid” addition was achieved by running in the calculated quality of NaOH from a pipette, a process which requires approximately 1 min. Rapid addition gives initially amorphous or nearly amorphous products as the initial product of precipitation. If the amorphous product is allowed to stand in contact with mother liquor at 0–100 °C, crystallisation occurs spontaneously, but the resulting product is often not ho-

Table 1
Precipitation conditions for $BiVO_4$ as functions of rate of pH change, final pH and ageing

Final pH ∼ 1, 1 h ageing of precipitate in mother liquor			
NaOH addition rate[a]	1.6, 17.6	24.2	Rapid
Final pH (±0.1)	1.00	1.15	1.00
Solid colour	Mustard Y	Pale Y	Peach/Y
Phases present	Z, S, F	Z	A
Final pH ∼ 1, but 24 h ageing of precipitate in mother liquor			
Final pH (±0.1)	1.10	1.00	1.10
Solid colour	Y	Pale Y	Peach/Y
Phases present	Z, F	A	Z
Final pH ∼ 2, 1 h ageing of precipitate in mother liquor			
NaOH addition rate[a]	1.6, 17.6	24.2	Rapid
Final pH (±0.1)	2.00	2.10	1.90
Colour	Mustard Y	Pale Y	Y
Phases present	Z, S	Z, S, F	Z, S, F
Final pH ∼ 2, but 24 h ageing of precipitate in mother liquor			
Final pH (±0.1)	1.90	1.75	1.95
Solid colour	Orange/Y	Peach/Y	Mustard/O
Phases present	Z, S	Z	Z, S, F

Y: yellow, O: orange, Z: zircon, S: scheelite, F: Fergusonite.

[a] Addition rate is expressed in ml NaOH/min added to 1 l of mixed reactants (see text). Where two values are given, the phases content and colour remained unchanged within limits. “Rapid” additions were achieved by pipette addition.

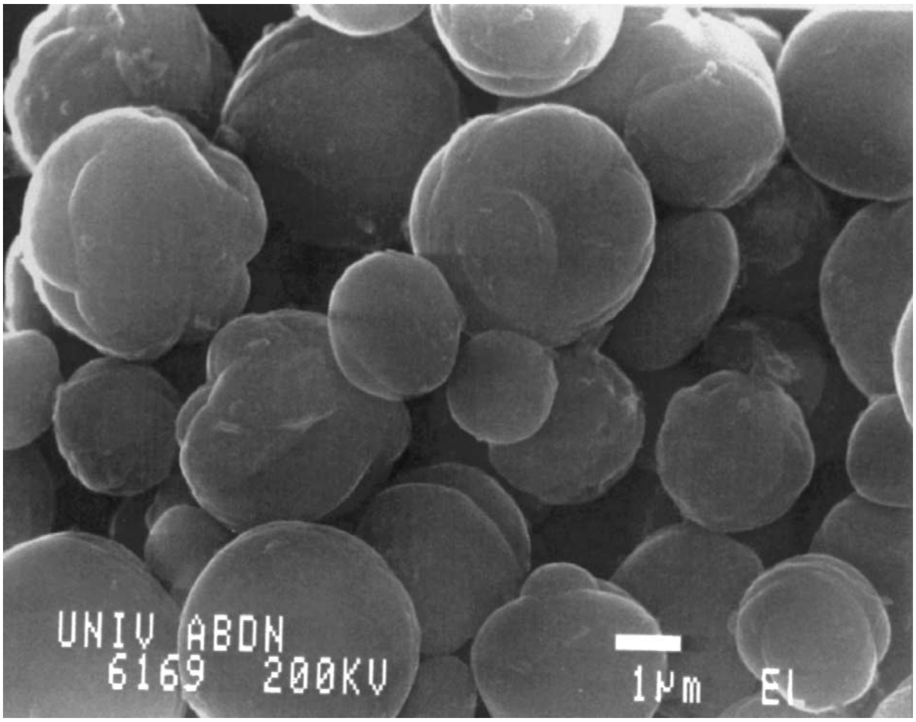

Fig. 2. Scanning electron micrograph of pigmentary grade $BiVO_4$ precipitated from acid solution.

mogeneous because differential precipitation occurs in the course of initial rapid precipitation, even when solutions are stirred.

2.2. Phase characterisation

Powder X-ray diffraction was used to identify crystalline phases. Depending on conditions, either zircon- or scheelite-structured products, or mixtures of the two, could be obtained, but we concentrate on the zircon-structured phase.

2.3. Microstructure

Fig. 2 shows the microstructure of the slowly precipitated and aged zircon-structured $BiVO_4$ product; it consists of numerous spherical or nearly spherical crystallites. Preparations vary in spherulite size but typically, individual preparations have only a narrow size distribution which is not significantly affected by ageing between 1 and 24 h. In the micrograph shown the spherulite size ranges between about 1 and 4 μm. Fig. 3 shows a representative transmission electron micrograph of one of the smaller spherulites from the same preparation illustrated in Fig. 2. The spherulites typically have low bulk density and occasionally have hollow cores. The spherulite walls have a composite texture, consisting of granular to fibrous crystallites, the latter often forming radial agglomerates of subparallel individual fibre-like crystallites. Electron diffractions confirm the zircon-structured, polycrystalline nature of the spherulites and that the constituent radial fibrous growths have little, if any, amorphous content after 1–24 h contact with mother liquor.

2.4. Thermal properties

Fig. 4 records thermal (DTA) and weight change (TG) data from an apparently single phase preparation of $BiVO_4$. This

Fig. 3. Transmission electron micrograph of one of the smaller spheres in Fig. 2, showing hollow core and fibrous, radiating structure.

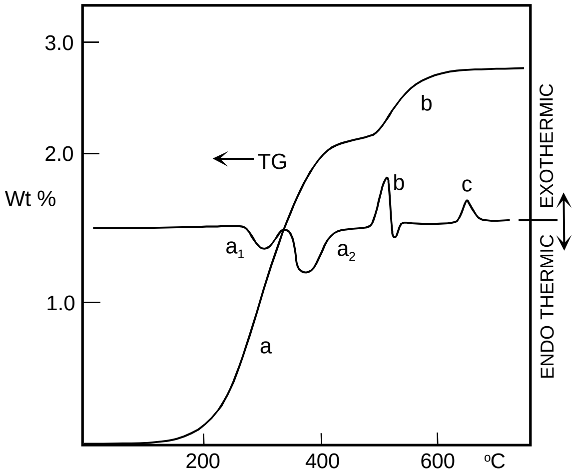

Fig. 4. Thermal activity (right hand scale) and mass change as percent of mass of air-dried $BiVO_4$ (105 °C). Heating rate 10 °C min in dry air. The first step corresponds to 2.0% loss and the second, higher temperature stage, to 0.78 wt. % loss.

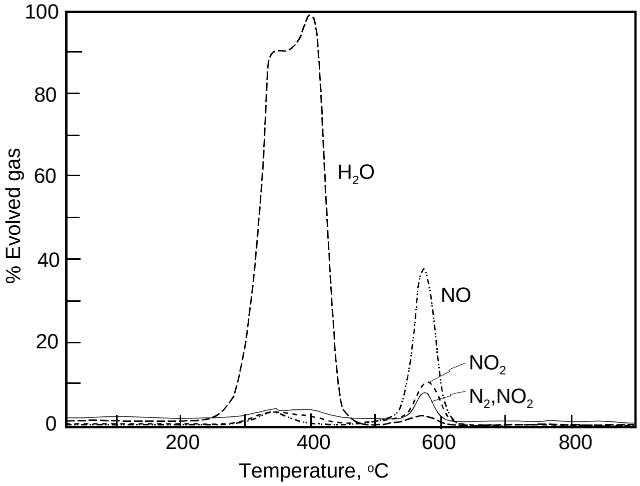

Fig. 5. Evolved gas analysis of a bright yellow, zircon-structured "$BiVO_4$". Two, possibly three, losses correspond to evolution of water at the lower temperature, 250–450 °C, and nitrogen oxide/nitrogen species at 520–610 °C. The water loss may occur in two completely resolved stages. The evolved species, shown as electrically neutral, were determined by mass spectroscopy. The maximum rate of evolution has been normalised to 100.

preparation had a particle size distribution and microstructure similar to that shown in Figs. 2 and 3. The DTA and TG data were complimented by (i) X-ray diffraction patterns obtained on a high-temperature stage and (ii) X-ray diffraction patterns obtained at ambient, ~20 °C, following static heating at selected temperatures, chosen with reference to Fig. 4, and rapid cooling. The heating experiments, DTA and TG, were made in dry air.

The complex series of events occurring in Fig. 4 is interpreted as follows: with rising temperatures the weight loss curve has two well-defined stages corresponding to 2.0 wt.% loss and 0.78%, respectively, relative to sample weight of air-dried material at 105 °C. Other phase pure preparations gave similar losses within ±5–10% of the stated loss. The differential thermal curve is more complex; the events designated a_1 and a_2 occur entirely within the region of the persistence of the zircon-structured phase (see Section 3 for additional interpretation). Event b is associated with transformation of the zircon-structured phase to the scheelite-structured phase. A further exothermic event, which is consistently encountered, but for which no explanation is presently available, occurs at ~600 °C.

Data were also obtained with programmed cooling (10 °C/min) but are relatively featureless. During cooling the scheelite-structured phase is known from X-ray diffraction to transform to the fergusonite type but the transformation is gradual, extending over a broad range of temperatures, with the result that the associated heat effect is too diffuse to be detected by thermal analysis. No mass changes occur during cooling and water is not regained spontaneously after long (5 years) contact with air.

Significant weight loss from a nominally anhydrous phase was a surprising and unexpected feature. The presence of significant amounts, approximately 2–3%, of physically trapped aqueous solvent was unlikely, given that the samples had been well dried at ~105 °C prior to thermal analysis. Moreover, the same two-stage loss pattern was consistently obtained from one zircon-structured preparation to another. Evolved gas analysis was used to identify the characteristic species giving rise to weight loss. Programmed heating was used (10 °C/min) to compliment the thermal analysis and the gas species were characterised by mass spectroscopy. Fig. 5 shows the composition of the evolved gas stream normalised to 100%. Two stages of gas evolution occur, temperatures of which correspond broadly to the two stages of weight loss recorded by TG. The gas evolved in the lower temperature range, 250–450 °C approximately, is primarily water while nitrogen-containing species, NO_2 and NO, dominate releases in the range 525–610 °C, approximately. There is a suggestion that the lower temperature release is complex and may consist of at least two incompletely resolved stages, in which case the two stages may correlate with the two endotherms, designated a_1 and a_2 in Fig. 4. Small but significant amounts of CO_2 appear to be evolved, although the near equivalence of the masses of CO_2 and N_2O makes it difficult to resolve unequivocally mixtures of the two.

2.5. Chemical analysis

It is apparent that the zircon-structured phase is not simply "$BiVO_4$" but instead has a more complex constitution. This prompted a re-analysis of the precipitated product with results for Bi and V as shown in Table 2; results are the means of a number of independent analyses made by classical wet-chemical methods. The product had been dried in air at 105 °C prior to analysis.

Table 2
Analysis of “$BiVO_4$”

Basis of calculation	Bi (wt.%)	V (wt.%)	Bi/V atomic ratio
Stoichiometric $BiVO_4$	64.516	15.727	1.000
Found, zircon type	61.02 ± 0.23	14.67 ± 0.08	1.014

The slightly bismuth-rich nature of the precipitated product relative to $BiVO_4$ stoichiometry is apparent and believed to be real. Indeed, a careful study of the X-ray patterns of the product obtained after heating the zircon-structured phase to ∼650 °C, resulting in its conversion mainly to a fergusonite-structured phase, invariably disclosed the presence of an additional set of weak reflections which are attributed to $Bi_4V_2O_{11}$, albeit with a few extra reflections which remain unassigned but are possibly due to superstructure in $Bi_4V_2O_{11}$. On the assumption that the fergusonite-structured phase is stoichiometric, a bismuth-rich precursor would be expected to develop a second phase high in bismuth and indeed, this is observed.

2.6. Crystallographic properties

The Bi:V ratio of typical preparations correlate with unit cell size of the zircon-structured phase and weight losses during heating. Table 3 shows the data which are complete for essentially single phase preparations. The total weight loss tends to diminish as the speed of precipitation increases but also, for a given speed of precipitation, to diminish with ageing between 1 and 24 h. It is also noteworthy that the higher temperature loss obtained from well-aged precipitates is still significant, ranging between 0.50 and 0.78 wt.%. The lattice parameters measured at 20 °C tend to decrease, albeit with some scatter, as the higher temperature weight loss decreases. The cell volume also appears to increase with ageing, although only one datum is available.

A reflectance infrared spectrum from $BiVO_4$ (zircon structure, dried at 105 °C but otherwise unheated) is shown in Fig. 6. The presence of water is indicated by a broad O–H stretch at approximately 3400 cm^{-1} with a corresponding bend at 1631 cm^{-1}. Structural hydroxyl groups also exhibit O–H stretching frequencies in the region 3000–3800 cm^{-1} and are believed to contribute to the broad band at about 3400 cm^{-1}. Features enabling the distinction between structural and absorbed water arise from the position of the O–H bend; for absorbed water a H–O–H bend typical occurs at 1600–160 cm^{-1} whereas for structural water, an M–O–H bend occurs below 1200 cm^{-1}, the exact position depending on the nature of the M species [21–23]. However, the strong V–OH stretch absorptions in this low frequency range precludes definite identification of possible V–OH and/or Bi–OH bends. Three V–O stretching frequencies are detected, at 927, 786 and 692 cm^{-1} whereas for undistorted VO_4 tetrahedral the corresponding single frequency would be expected to occur at 796 cm^{-1}.

2.7. Impact of grinding

It is well known that grinding pigmentary grade $BiVO_4$ intensifies in colour at least during the initial stages of grinding. In the course of the present study, numerous preparations were dry ground by hand in an agate mortar and pestle. Prolonged grinding, even of the gentle nature associated with grinding by hand, readily initiates transformation of the zircon-structured phase to the scheelite type. With small (approximately 500 mg) samples, transformation was virtually complete in approximately 15–30 min. If, on the other hand, the powder was moistened to a paste with water prior to grinding, the transformation was much slower. Initially, brighter colours were obtained as agglomerates were disaggregated. However, as transformation to the scheelite-structured phase occurred, the colours became muddy, tending towards brown. Colour arises from many

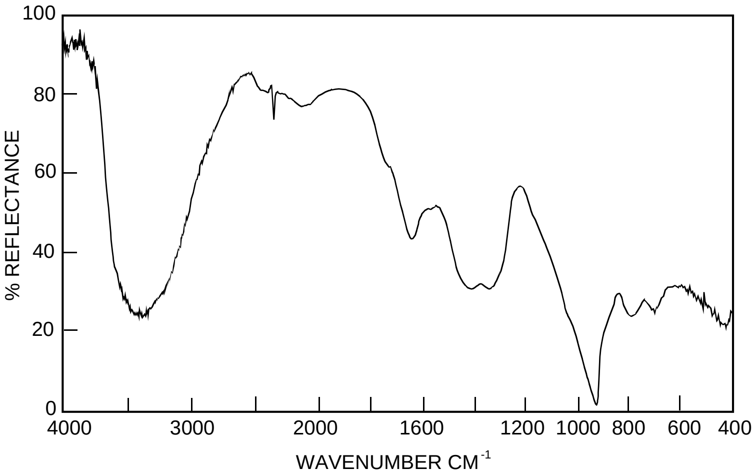

Fig. 6. Reflectance spectra of a bright yellow, zircon-structured “$BiVO_4$” preparation. The sample was dried at 100 °C but was otherwise unheated. The sample was unground, as grinding is known to result in partial phase transformation (see text for an explanation of the spectra). The small sharp spike at ∼2250 cm^{-1} is believed to be an artefact.

Table 3
Lattice parameters and volatile fraction of precipitated zircon-structured $BiVO_4$

	Rate of NaOH addition (ml/min)		
	0.40	1.21	Rapid
Brief 91 h ageing of precipitate in contact with mother liquor			
Initial pH	1.05	1.20	
Product characteristics			
Total weight loss (%)	2.96	2.78	2.30
First stage (130–480 °C)	2.08	2.00	1.94
Second stage (480–633 °C)	0.88	0.78	0.36
Exotherm (°C)	517	51	490
Endotherms (°C)	238.381	227–399	217–410
	515–524	510–519	479–497
	703	701	700
Product composition			
Bi (%)	60.84 (18)	61.02 (23)	60.99 (17)
V (%)	14.34 (9)	14.67 (8)	14.93 (7)
Bi:V ratio	1.031	1.014	0.996
Unit cell parameters			
a (Å)	7.3066 (5)	7.3016 (8)	7.2999 (4)
c (Å)	6.4608 (9)	6.4527 (12)	6.4550 (5)
Volume ($Å^3$)	344.91	344.02 (8)	343.98 (4)
	Rate of NaOH addition (l/min)		
	0.40	1.21	Rapid
24 h ageing of precipitate in contact with mother liquor			
Initial pH	1.15	1.05	1.10
Product characteristics			
Total weight loss (%)	2.62	2.63	2.03
First stage (135–69 °C)	1.90	1.82	1.53
Second stage (480–633 °C)	0.71	0.78	0.50
Exotherm (°C)	4.99	509	464
Endotherms (°C)	218–395	231–389	205–429
	489–505	504–517	445–487
	699	702	663
Product composition			
Bi (%)	61.05 (14)	–[a]	–[a]
V (%)	14.64 (8)	–[a]	–[a]
Bi:V ratio	1.017	–[a]	–[a]
Unit cell parameters			
a (Å)	7.3213	–[a]	–[a]
c (Å)	6.9721 (28)	–[a]	–[a]
Volume ($Å^3$)	346.91 (20)	–[a]	–[a]

Temperature ranges varied within the limits.

[a] Not single phase.

causes [24] and, in this instance, is influenced by preparation, stochiometry and grinding.

3. Discussion

Results of the present study raise a number of questions. Firstly, why should phase relations differ so much between the $ZrSiO_4$ and $BiVO_4$ systems? At the $ZrSiO_4$ composition the zircon-structured phase is stable across a broad range of temperatures and pressures. Only at very high pressures, in the range 30–53 GPa, does it convert to the scheelite-structured phase. The density contrast is significant: the scheelite type is about 10% denser than the zircon type [25–27]. Similar density relationships obtain for $BiVO_4$, yet on heating the zircon-structured phase at 1 bar pressure, it spontaneously converts to the denser scheelite type. This is an unusual state of affairs because heating, by increasing the thermal amplitude of vibration, generally favours formation with rising temperatures of low density phases; here the inverse relationship obtains. Stabilisation of the zircon structure is probably achieved by partial substitution of (OH,NO_3) for vanadate polyhedra with concomitant changes in Bi:V ratio. The space required for their inclusion favours the larger molar volume zircon structure type; their elimination allows transformation to the denser scheelite type.

A second noteworthy features is the occlusion and retention to high temperature (>180 °C) of NO_3^- and OH^- in the zircon-structured precipitate and of the structural role of these anions. Measured on preparations dried at 105 °C, the loss amounts to ∼2% or more of the dry weight and is thus significant. The largely structural nature of the incorporation is disclosed by the comparison of the weight loss curve with thermal analysis curves and X-ray diffractions after heating to selected temperatures. The weight loss curve reveals apparently two discrete stages of weight loss. The lower temperature loss occurs across a fairly broad temperature range and is almost completely resolved from the higher temperature loss; the latter is comparatively sharp but has less total loss than the lower temperature stage. This higher temperature loss also correlates well with the DTA, which gives a single and comparatively sharp associated endotherm. However, the thermal activity in the temperature range of the lower temperature loss is more complex. Two interpretations of the differential thermal pattern are possible: that two endotherms occur or, alternatively, that the thermal activity results from a combination of events: a broad endotherm on which is superimposed a relatively sharp exothermic event.

The second explanation, of a combination of events, provides a good fit to the shape of the weight loss curve and the known crystallographic transformation. In this explanation the origin of the exothermic event is attributed to a combination of processes; reycrstallisation of the zircon-structured phase to scheelite as well as gas phase reactions between the evolved species and the flowing atmosphere (air). In this context, it should be recalled that one of the evolved gas phase constituents, N_2O, is combustible giving rise to an exothermic reaction. The apparently single, smooth weight loss might conceal detail, but if so we have not been successful in resolving it. We therefore prefer the second explanation, of a single broad endotherm upon which is superimposed a relatively sharp exotherm.

The structural incorporation of anions such as OH in silicate structures has considerable precedent. A well-known example is of OH^- substitution into grossularite, $Ca_3Al_2Si_3O_{12}$. In this instance the end member, hydrogrossularite, $Ca_3Al_2(OH)_{12}$ is readily synthesised from aqueous solution at 1 bar pressure in the temperature range 20–100 °C. Although miscibility between grossularite and hydrogrossularite is incomplete at 1 bar pressure, the formal mechanism of solid solution is clear: $4OH^-$ replaces SiO_4^{4-} [28–32]. However, the location of hydrogens remains elusive: in hydrogarnet, as in zircon, it is not necessary that the $4OH^-$ reside physically in the space formerly occupied by SiO_4^{4-}. Thus it would appear that in zircon-structured $BiVO_4$, formal replacement of VO_4^{3-} by $(OH,NO_3)_3$ occurs in the course or precipitation. Since the formal change of VO_4 is only 3^-, fewer (OH,NO_3) ions per XO_4 unit are required for charge balance than in hydrogarnet. The suggested mechanism would also accord with the excess of Bi over V found by chemical analysis, although such agreement does not of itself constitute proof. In the present example, as in hydrogarnet, the low scattering power of hydrogen for X-rays precludes application of Rietveld refinement to the X-ray patterns to determine the extent of ordering of hydrogen and its locations within the structure. It might be useful to synthesise deuterated versions of the structure with a view to applying diffraction and infrared spectral measurements to the more accurate determination of light atom positions and hence determining the mechanism of substitution. However, as noted, the distribution of OH replacing SiO_4 in mineral structures is not as yet established and the experimental problems associated with determining anion locations are considerable.

As prepared, the Bi:V ratio of the zircon-structure phase is somewhat variable but many preparations, typically those with good yellow colour, have a chemical excess of Bi over V. One mechanism of achieving nonstoichiometry is to alter the oxidation states of the constituent elements, both Bi and V having states other than the nominal (III) and (V) states. However, the precipitation medium is HNO_3, an oxidising acid, and in the absence of other reductants, it is supposed that V is uniformly in its upper (V) oxidation state. Bismuth is more problematic but Bi(V) is probably only obtained significant quantities in alkaline solution in the presence of a strong oxidising agent. Experience of heating and cooling preparations in an oxidising atmosphere, air, does not suggest that the complex weight changes are associated with changes to the normal oxidation states. Thus, Bi and V are believed to remain in this “normal”, i.e., Bi(III) and V(V) states throughout the course of experiments made in oxidising aqueous media or in air.

The chemical nature of the zircon- and scheelite-structured phases is complex and it is apparent that the interconversion of phases and lack of reversibility upon heating and cooling implies that any thermodynamic treatment of phase stability in terms of the one component system $BiVO_4$ would be inappropriate. The content of exotic anions, NO_3 and OH^-, presumably provides extra thermodynamic stabilisation for the low density zircon-structured phase. Indeed, we are unable to find evidence for the existence of a zircon structure phase in this system without the presence of ions such as OH^- and NO_3^-.

With respect to the practical implications, it is apparent that $BiVO_4$ pigments are often used in products which undergo thermal processing. Heating is likely therefore to induce a complex series of phase transformations and weight loss in precipitated products owing to evolution of structural nitrate and hydroxyl in the form of nitrogen, nitrogen oxides and water. Thus, gas evolution may affect the matrix. Moreover, the changes in symmetry occurring during heating and cooling of the pigment allow twinning to develop internally, within crystallites. Thus, the interaction of twin domain boundaries, defect content induced by thermal, chemical and polymorphic phase changes and the possible exsolution of a Bi-rich phase are likely to affect colour and these influences will be superimposed on those due to particle size and morphology. We are as yet some way from being able to quantify and control the colour of $BiVO_4$: the present paper highlights the complexities of the problems and warns against too simplistic an approach but points the way forward.

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