Energetics of Bismuth Vanadate

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Abstract

Bismuth vanadate has gained considerable interest as a photoanode for water splitting reactions under visible light. It exists in four different polymorphs, out of which three of them have been synthesized. Thermodynamic properties of these three polymorphs are investigated using high temperature oxide melt solution calorimetry. The monoclinic scheelite phase which exhibits photocatalytic activity under visible light is found to be the most stable polymorph, followed by tetragonal scheelite which exhibits activity under UV light. The photocatalytically inactive tetragonal zircon form is found to be the least stable polymorph. The small difference in enthalpy of formation between the two scheelite structures (-8 kJ/mol) is in accord with the reversibility of the transformation between them and the larger difference between the most stable monoclinic phase and the least stable tetragonal zircon phase (-23 kJ/mol) is in accord with the irreversible (monoclinic $\rightarrow$ tetragonal zircon) phase transformation.

Introduction

Solar water splitting has gained considerable attention as an attractive way to convert solar energy into a chemical fuel in the form of hydrogen [1]. Semiconductor photocatalysts have shown exceptional activity in solar energy conversion. TiO_2 has shown extensive photocatalytic activity under UV light and has been widely used due to its distinctive chemical inertness, non toxicity, resistance to photocorrosion and low cost [2]. The need for an alternative, visible light photocatalyst arises because the solar spectrum consists of only 4 % UV light, and therefore the efficiency of TiO_2 photocatalysts under solar irradiation is very low. Bismuth vanadate (BiVO_4) is one such material and is found to be a promising candidate for water splitting and organic pollutant decomposition under visible light irradiation [3-6]. It is potentially useful in many fields owing to its unique properties including ferroelasticity, photochromic effect and ionic conductivity [7-8]. These properties are dependent on the type of polymorph, structure and microstructure of BiVO_4 . Among the other known polymorphs, clinobisvanite polymorph (monoclinic scheelite) is known to exhibit excellent photocatalytic activity and photoelectrochemical behavior.

BiVO_4 occurs as a mineral in three polymorphs, orthorhombic pucherite, tetragonal dreyerite, and monoclinic clinobisvanite [9]. All have tetrahedrally coordinated vanadium and eight-fold coordinated bismuth. The first described polymorph was pucherite [10], which is the most abundant. Its structure is orthorhombic with space group $Pnca$ and the lattice parameters: $a = 5.328(2)$, $b = 5.052$ and $c = 12.003(3)$ Å at 291 K [11]. The tetragonal polymorph, dreyerite, has been reported from only one locality in rhyolitic tuffs [12]. Its structure is tetragonal, with space group $I4_1/amd$ and $a = 7.303(3)$ $c = 6.584(3)$ Å. Monoclinic clinobisvanite occurs in pegmatites as an oxidation product of other bismuth minerals [13]. Its structure is monoclinic, space group $I2/a$, with $a = 5.195$, $b = 11.701$, $c = 5.092$ Å and $\beta = 90.38^\circ$ [13]. While the laboratory syntheses of monoclinic clinobisvanite and tetragonal

dreyerite are known, the orthorhombic pucherite is only known to exist in nature. In addition to these three polymorphs, BiVO_4 is also known to crystallize in the tetragonal scheelite structure in laboratory synthesis [14].

The inter-polymorphic phase transformations in BiVO_4 are well documented in the literature. A schematic representation of several transformations is shown in Fig.1. Tetragonal zircon BiVO_4 (BV-tz) irreversibly transforms to monoclinic scheelite BiVO_4 (BV-ms) upon heating to 400 - 500 °C [15]. On the other hand, the phase transformation between monoclinic scheelite BiVO_4 and tetragonal scheelite BiVO_4 (BV-ts) occurs reversibly at 255 °C [16-17]. This reversible transformation is well studied using several techniques including in situ neutron diffraction and Raman spectroscopy, since the transition is associated with change in elastic properties [18-19].

Fig 1. Schematic representation of polymorphic transitions in BiVO_4

Despite their interesting properties and phase transitions, there are no thermodynamic data reported for BiVO_4 polymorphs except for a report on calculation of the enthalpy of formation of monoclinic BiVO_4 using density functional theory (DFT) [20-21]. In the current paper we report the synthesis of the three polymorphs of BiVO_4 and their experimental

formation and transformation enthalpies determined using high-temperature oxide melt solution calorimetry. We discuss these findings in terms of phase stability and metastability.

Experimental Methods

Synthesis

Monoclinic scheelite BiVO_4 (BV-ms) was prepared by solid state synthesis [22]. A 1:1 ratio of $\text{Bi}(\text{NO}_3)_3$ and NH_4VO_3 were ground in agate mortar. The mixture was then heated for 24 hrs at 120 °C. The sample at this stage comprised a mixture of monoclinic and tetragonal zircon phases. It was then heat treated at 700 °C for 8 h to obtain the pure monoclinic phase.

Tetragonal scheelite BiVO_4 (BV-ts) was prepared by a simple precipitation method [23]. 4.85 g of $\text{Bi}(\text{NO}_3)_3$ and 2.21 g of Na_3VO_4 were separately dissolved in 70 mL of 2 M nitric acid.. The solutions were mixed to get a pale yellow colour solution to which 7 g of Na_2CO_3 was added, followed by stirring for 6 h. The sample was dried at 100 °C for 5 h.

Tetragonal zircon BiVO_4 (BV-tz) was also prepared by a simple precipitation method [24]. 2.21 g of NH_4VO_3 was dissolved in 250 mL distilled water under stirring at 50 °C. 5.82 g of $\text{Bi}(\text{NO}_3)_3$ was added and the system left under stirring for 2 h.. Then the solution containing a precipitate was sonicated for 15 min before filtration followed by drying at 100 °C for 5 h.

Characterization

Powder X-ray diffraction (PXRD) of all samples was recorded using a Bruker-AXS D8 Advance diffractometer operated at 40 kV and 40 mA using Cu-K α radiation. Lattice parameters and crystallite sizes were calculated by whole pattern profile fitting using General Structure Analysis System (GSAS) software [25]. Thermogravimetric (TG) analysis was performed using a Netzsch 449 TG/DSC instrument under 1 bar Ar atmosphere (25 °C–500

°C, heating rate 5 °C/min, Pt crucible). Temperature programmed desorption mass spectrometry analysis were performed on a Labsys Evo instrument coupled with mass spectrometry. The TPD exhaust species were collected into the ionization chamber of a Micromeritics cirrus 2 quadrupole mass spectrometer, ionized and fragmented by electron impact. The data were analyzed using Netzsch Proteus software. A Bruker Equinox 55 FTIR spectrometer (range 400 - 4000 cm⁻¹) operated with Opus software was used to collect IR spectra of the samples. The specific surface area was measured by the Brunauer-Emmett-Teller (BET) method using a Micromeritics Gemini VII surface area analyzer. The samples were degassed at 100 °C for 5 h before measurement

High-Temperature Oxide Melt Solution Calorimetry

High temperature oxide melt solution calorimetry was performed using a custom-built isoperibol Tian-Calvet microcalorimeter as described by Navrotsky [26-27]. Molten sodium molybdate (3Na₂O·4MoO₃) was used as solvent at 700 °C. The calorimeter was calibrated using the heat content of high purity α -Al₂O₃. Oxygen was flushed through the glassware at 35 mL/min to maintain constant atmosphere and bubbled thorough the solvent at 4.5 mL/min to maintain oxidizing conditions, to aid dissolution, and to prevent local saturation of the solvent. In a typical experiment ~5 mg of sample was pelletized and dropped into the solvent. The resulting heat effect (heat of drop solution, ΔH_{ds}) includes the heat content of the oxide, the heat effect associated with desorbing and heating any adsorbed surface water, and the heat of dissolution of oxide in the high-temperature solvent. Heats of drop solution of the binary oxides were taken from recent published work [28-29]

Results and Discussion

The PXRD pattern of all the three polymorphs of BiVO₄ is shown in Fig. 2. The refined lattice parameters are given in Table 1. The PXRD patterns of the *ms*-BiVO₄ (Fig 1a)

and *ts*-BiVO₄ phase (Fig 1b) differs very slightly. Splitting of the peaks at $2\theta = 18.5, 35$ and 46° confirms the monoclinic phase [14]. The PXRD pattern in Fig 1c could be fitted to the tetragonal zircon phase, with its characteristic peaks at $2\theta = 24.4$ and 32.7° [15]. The crystallite sizes of all the polymorphs were calculated by classical linear Williamson-Hall plot using X'Pert HighScore Plus software and are listed in Table 1.

Figure 2. Profile fitting of PXRD patterns of BiVO₄ (a) BV-ms (b) BV-ts and (c) BV-tz polymorphs

BiVO₄-ms exhibits a specific surface area of 2.25 m²/g which is higher than the 1.24 m²/g for BiVO₄-tz and 0.13 m²/g for BiVO₄-ts. Nevertheless all three samples can be considered bulk, rather than nanophase, materials in terms of energetics. .

Table 1. Refined lattice parameters, calculated crystallite size and measure surface area of the three polymorphs of BiVO₄

BiVO ₄	Cell parameters (Å)				Size (PXRD) nm	Surface area m ² /g
	a	b	c	β		
<i>BV-ms</i>	5.193(5)	5.089(8)	11.697(2)	90.38	680	2.25
<i>BV-ts</i>	5.150(9)	5.150(9)	11.730(1)	90.00	287	0.13
<i>BV-tz</i>	5.147(1)	5.147(1)	11.721(6)	90.00	219	1.24

Fig 3 shows the IR spectra of all three samples. Bands observed at 1020 and 860 cm⁻¹ for BV-ms (Fig 3a) could be assigned to the asymmetric stretching vibration (ν_3) and symmetric stretching vibration (ν_1) of VO₄ units respectively [30]. Overlapping bands observed at 620 to 680 cm⁻¹ could be assigned to Bi-O stretching modes and the one at 470 cm⁻¹ to the bending mode (ν_4) of VO₄ units. BV-ts (Fig 3b) sample does not show any distinguishable features but one broad band where the bending and stretching modes are merged. This is known to be characteristic of the tetragonal phase [31]. Along with this broad band an additional feature is observed at 1380 cm⁻¹, which can either be assigned to adsorbed nitrate from the synthesis or adsorbed atmospheric carbonate. BV-tz shows similar features with a broad band in the range of 450 to 950 cm⁻¹, corresponding to VO₄ stretching and

bending modes. The band at 1380 cm^{-1} could be due to adsorbed nitrate impurity as the synthesis involved the use of nitrate precursor.

Figure 3. IR spectra of (a) BV-ms, (b) BV-ts and BV-tz samples

TG-DSC curves of all three samples are shown in Fig 4. TG curve corresponding to BV-ms (Fig 4a) does not show any mass loss indicating the absence of adsorbed water or any other volatile impurities. It does not exhibit any prominent feature at $300\text{ }^{\circ}\text{C}$ where there could be a phase transition from monoclinic to tetragonal scheelite phase. BV-ts shows a total mass loss of 1.4 %. This small mass loss observed can be attributed to adsorbed water and nitrate impurities as seen in the IR spectrum of this sample. This was also confirmed by evolved gas analysis using mass spectroscopy (Fig. 4b). BV-tz shows a continuous mass loss of 5 % up to $500\text{ }^{\circ}\text{C}$, which could be attributed to adsorbed water and nitrate impurities as evidenced in IR spectrum of this sample (Fig. 3c) and also confirmed by mass spectroscopy

(Fig 4c) [32]. However we do not see any appreciable changes in DSC at 400 – 500 °C, where BV-tz transforms irreversibly to BV-ms.

Figure 4. TG-DSC curves of BiVO₄ powders (a) BV-ms (b) BV-ts and (c) BV-tz high temperature oxide melt solution calorimetry

The enthalpies of formation of bismuth vanadate at 25 °C from constituent oxides ($\Delta H_{f,ox}$) were calculated using thermochemical cycle shown in Table 2.

Table 2. Thermochemical cycle used for the calculation of enthalpy of formation of BiVO_4

Enthalpy of formation of Bismuth vanadate		
$\text{BiVO}_4 \text{ (s, 25 } ^\circ\text{C)} \longrightarrow \text{BiO}_{1.5} \text{ (Soln., 702 } ^\circ\text{C)} + \frac{1}{2} \text{V}_2\text{O}_5 \text{ (Soln., 702 } ^\circ\text{C)}$		$\Delta H_{ds} \text{ (1)}$
$\text{BiO}_{1.5} \text{ (s, 25 } ^\circ\text{C)} \longrightarrow \text{BiO}_{1.5} \text{ (Soln., 702 } ^\circ\text{C)}$		$\Delta H_{ds} \text{ (2)}$
$\text{V}_2\text{O}_5 \text{ (s, 25 } ^\circ\text{C)} \longrightarrow \text{V}_2\text{O}_5 \text{ (Soln., 702 } ^\circ\text{C)}$		$\Delta H_{ds} \text{ (3)}$
$\text{BiO}_{1.5} \text{ (s, 25 } ^\circ\text{C)} + \frac{1}{2} \text{V}_2\text{O}_5 \text{ (s, 25 } ^\circ\text{C)} \longrightarrow \text{BiVO}_4 \text{ (s, 25 } ^\circ\text{C)}$		$\Delta H_{f,ox} \text{ (4)}$
$\Delta H_{f,ox} \text{ (4)} = - \Delta H_{ds} \text{ (1)} + \Delta H_{ds} \text{ (2)} + 0.5 \Delta H_{ds} \text{ (3)}$		

$\Delta H_{f,ox}$ – formation enthalpy from oxides, ΔH_{ds} – enthalpy of drop solution

Figure 5. Enthalpy of formation of different polymorphs of BiVO_4

The calculated enthalpies of formation for BV-ms, BV-ts and BV-tz were -93.02 ± 2.18 , -84.88 ± 1.65 and -69.91 ± 0.88 kJ/mol respectively (Fig.5). According to our experimental results the enthalpy of formation for BV-ms is more exothermic followed by BV-ts and BV-tz which is least exothermic. Calorimetric data and the enthalpy of formation data are given in Table 3.

Table 3. Thermochemical data for the three polymorphs of BiVO_4

Phase	$\Delta H_{\text{ds}}(\text{kJ/Mol})$	$\Delta H_{\text{f, oxd}}(\text{kJ/Mol})$
BV-ms	$168.23 \pm 1.65(6)$	-93.02 ± 2.18
BV-ts	$160.09 \pm 0.88(6)$	-84.88 ± 1.65
BV-tz	$145.12 \pm 2.18(6)$	-69.91 ± 0.88

As shown in Figure 1 both the tetragonal polymorphs transform to the monoclinic form and our results confirm that this is the most stable phase. In all three polymorphs V is tetrahedrally coordinated to four O atoms and Bi forms dodecahedra with eight O atoms as shown in Fig 6. In the scheelite structure (BV-ms and BV-ts), each BiO_8 dodecahedral unit is surrounded by eight VO_4 units and each O atom is coordinated to two Bi and one V atom. The only difference between the two scheelite structures is that, in the monoclinic polymorph there is local distortion around Bi and V atoms resulting in the loss of four-fold symmetry. This is reflected in the difference in bond lengths between these two structures. In tetragonal scheelite, all four V-O bond lengths are equal ($1.73 \text{ \AA}$), and only two different Bi-O bond lengths exist (2.4 and $2.47 \text{ \AA}$). On the other hand, there are two different V-O bond lengths (1.69 and $1.76 \text{ \AA}$) and four different Bi-O bond lengths (2.35 , 2.37 , 2.52 and $2.63 \text{ \AA}$) in the monoclinic scheelite structure.

Figure 6. Crystal structures of (a) BV-ms, (b) BV-ts and (c) BV-tz polymorphs

These slight changes in structure between these two polymorphs are reflected in the relatively small difference (8.14 kJ/mol) in their enthalpy of formation. This small difference is also consistent with reversibility of transformation of these two polymorphs. While the monoclinic polymorph is stable at room temperature, tetragonal scheelite is formed at 255 °C [16-17]. However in laboratory syntheses these two polymorphs can be synthesized in pure

form under different conditions easily and it is not clear whether 255 °C represents the equilibrium transformation temperature.

On the other hand in the tetragonal zircon structure each BiO_8 dodecahedral unit is surrounded by six VO_4 units. While two O atoms of two VO_4 units are bonded to Bi, the other four VO_4 units provide one O atom each to the BiO_8 dodecahedron. Tetragonal polymorph is known to irreversibly transform to the monoclinic phase at 400 - 500 °C [15] and hence is generally synthesized at lower temperatures. The enthalpy of this transformation is -23 kJ/mol, confirming that the tetragonal phase is metastable.

Thus the stability of the three laboratory synthesized polymorphs of BiVO_4 varies in the order BV-ms – BV-ts – BV-tz, with monoclinic being the most stable phase. Further the monoclinic polymorph of BiVO_4 is known to be the only phase among the other three to exhibit excellent photocatalytic activity under visible light, while tetragonal scheelite exhibits moderate photocatalytic activity in UV light and tetragonal zircon is photocatalytically inactive. The thermodynamic measurements show that the most interesting phase from the point of view of photocatalysis is also the thermodynamically stable form. This eliminates any concerns about phase transformations from the monoclinic phase to other less active forms during operation of the photocatalyst.

Conclusion

Formation enthalpy of three laboratory synthesized BiVO_4 polymorphs are calculated using the data obtained from high temperature oxide melt solution calorimetry. The photocatalytically active monoclinic scheelite polymorph is the most stable followed by tetragonal scheelite polymorph and tetragonal zircon polymorph. The slight change in the structures of the two scheelite phases is reflected in the small differences in their formation enthalpy and the reversibility of transformation between the two.

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Schematic representation of polymorphic transitions in BiVO_4 along with their formation enthalpies.