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Crystal Structure of the High-Pressure Form of BiVO_4

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The crystal structure of BiVO_4 , which has a monoclinic, distorted scheelite structure at ambient conditions, has been determined above the high-pressure transition at 1.6 and 4.3 GPa, and 23°C. At these pressures BiVO_4 has the tetragonal scheelite structure, which is also observed at high temperature above 250°C at room pressure. Vanadium tetrahedra remain rigid with no significant change in size at high pressure. Reduction of unit-cell volume is principally a result of Bi-O polyhedral compression. This behavior is similar to that observed for other scheelite-type compounds, in which tetrahedra are rigid and compression occurs in the 8-coordinated polyhedron.

KEYWORDS Bismuth vanadate; scheelite, isomorphs; ferroelastic transitions; crystal structure, high-pressure; pressure, phase transformations.

INTRODUCTION

Bismuth vanadate has attracted considerable attention in recent years since it was observed to undergo a ferroelastic, monoclinic-to-tetragonal phase transition at approximately 250°C (Bierlein and Sleight, 1975). Raman and Brillouin spectroscopy at high temperature (Pinczuk *et al.*, 1977; Tokumoto and Unoki, 1983) have led to the

conclusion that BiVO_4 displays a "pseudo-proper" phase transition belonging to the ferroelastic species $4/mF2/m$, in the terminology of Aizu (1969).

The high-pressure behavior of BiVO_4 was first examined by Pinczuk *et al.* (1979) with Raman spectroscopy. Their results indicate that BiVO_4 , which at ambient conditions is monoclinic (space group $I2/a$) with a distorted scheelite structure, transforms to the tetragonal scheelite form ($I4_1/a$) at pressures greater than 1.40 ± 0.05 GPa at room temperature. Combined high-pressure and high-temperature birefringence measurements (Wood *et al.*, 1980) indicate a linear relationship between T_c and pressure ($dP/dT = -0.0062$ GPa/ $^\circ\text{C}$). This observation was confirmed by the high-pressure measurements and the simultaneous high-pressure and high-temperature measurements of Hazen and Mariathasan (1982). The objective of the present high-pressure work on BiVO_4 is to document structural variations that might reveal mechanisms of the tetragonal-to-monoclinic transition.

EXPERIMENTAL

Synthetic single crystals of BiVO_4 were cut from a boule supplied by the Royal Signals and Radar Establishment (Malvern, G.B.). The crystal used for structure determination, a (110) plate approximately $90 \times 90 \times 30$ μm , was the same as that described by Hazen and Mariathasan (1982) for lattice-parameter determinations. The crystal was mounted in a diamond-anvil, high-pressure cell for single-crystal, x-ray diffraction, and a 4:1 methanol:ethanol mixture was used as the hydrostatic-pressure transmitting fluid. Ruby chips were included in the mount for pressure calibration. Details of procedures for crystal mounting, crystal centering on a four-circle diffractometer, unit-cell determination, and data collection are described by Hazen and Finger (1982).

Intensity measurements were made on an automated four-circle Picker diffractometer with Nb-filtered $\text{MoK}\alpha$ radiation. The constant-precision intensity technique described by Finger *et al.* (1973) and the fixed- ϕ mode of high-pressure data collection (Finger and King, 1978) were employed. Corrections for absorption by the diamond cell were made automatically, and the diffraction peak profiles were individually

TABLE I
Conditions of refinement for BiVO_4 at
1.6 and 4.3 GPa

Parameter	1.6 GPa	4.3 GPa
a (Å)	5.105(1)	5.080(2)
c (Å)	11.577(1)	11.490(1)
V (Å ³)	301.7(1)	296.5(2)
No. observed refl.		
$I > 2\sigma$	128	136
R (%)	4.8	5.1
w R (%)	4.7	4.4

examined after data collection. This procedure results in background levels that can be checked and reset manually when required. Reflections overlapped by white radiation streaks from the diamonds were rejected. Refinement was accomplished with the program RFINE (Finger and Prince, 1975). The high-temperature structure reported by David *et al.* (1979) was used for initial atomic parameters. The initial refinement, which included anisotropic temperature factors for the metal ions, yielded an R of 4.6%.

DISCUSSION

High-pressure crystal chemistry

The high-pressure structure of BiVO_4 , as expected from the high-pressure Raman and birefringence results, is very similar to the high-temperature structure, both of which are isostructural to scheelite (tetragonal, space group $I4_1/a$). Conditions of refinement appear in Table I, and refined structural parameters are recorded in Table II.† The high-pressure structures can be compared with the high-temperature structures of David *et al.* (1979) by plotting lattice parameters as a function of relative unit-cell volume (i.e., the volume

† Tabulated observed and calculated structure factors for BiVO_4 at 1.6 and 4.3 GPa are available from the authors on request.

TABLE II
 Refined structural parameters for tetragonal BiVO₄ at 1.6 and 4.3 GPa

Atom	Parameter	1.6 GPa	4.3 GPa
Bi	<i>x</i>	0	0
	<i>y</i>	$\frac{1}{4}$	$\frac{1}{4}$
	<i>z</i>	$\frac{5}{8}$	$\frac{5}{8}$
	$\beta_{11} = \beta_{22}$	0.0099(5)	0.0083(5)
	β_{33}	0.0014(1)	0.0011(1)
	$\beta_{12} = \beta_{13} = \beta_{23} = 0$		
V	<i>x</i>	0	0
	<i>y</i>	$\frac{1}{4}$	$\frac{1}{4}$
	<i>z</i>	$\frac{5}{8}$	$\frac{5}{8}$
	$\beta_{11} = \beta_{22}$	0.0081(15)	0.0091(16)
	β_{33}	0.0015(3)	0.0016(4)
	$\beta_{12} = \beta_{13} = \beta_{23} = 0$		
O	<i>x</i>	0.143(3)	0.142(3)
	<i>y</i>	-0.001(3)	-0.002(3)
	<i>z</i>	0.203(1)	0.204(1)
	β_{11}	0.007(7)	0.004(7)
	β_{22}	0.019(7)	0.016(7)
	β_{33}	0.0012(8)	0.0016(8)
	β_{12}	0.001(4)	-0.003(4)
	β_{13}	-0.000(2)	0.001(2)
	β_{23}	0.001(2)	0.001(2)

of the unit cell relative to that of the structure at ambient room conditions). Such a plot is given in Figure 1, where a linear relationship between unit-cell edges and relative volume, *independent* of temperature and pressure, is observed. The fractional coordinates of oxygen remain almost constant in the high-temperature and high-pressure phases.

Comparison of the bismuth and vanadium cation polyhedra as functions of temperature and pressure reveals that the vanadium tetrahedron is very rigid. Vanadium-oxygen bond lengths remain approximately constant between 1.6 and 4.3 GPa and are similar in the high-temperature and high-pressure refinements, with a mean V-O distance of $1.72 \pm 0.01 \text{ \AA}$. The V-O distance in the monoclinic phase at normal temperatures and pressures, furthermore, is the same as in the tetragonal phase. The bismuth 8-coordinated polyhedron, on the other hand, is far less rigid, and the mean Bi-O bond compresses approximately 1% between 1.6 and 4.3 GPa (Table III). These observations are consistent with the hypothesis that the behavior of

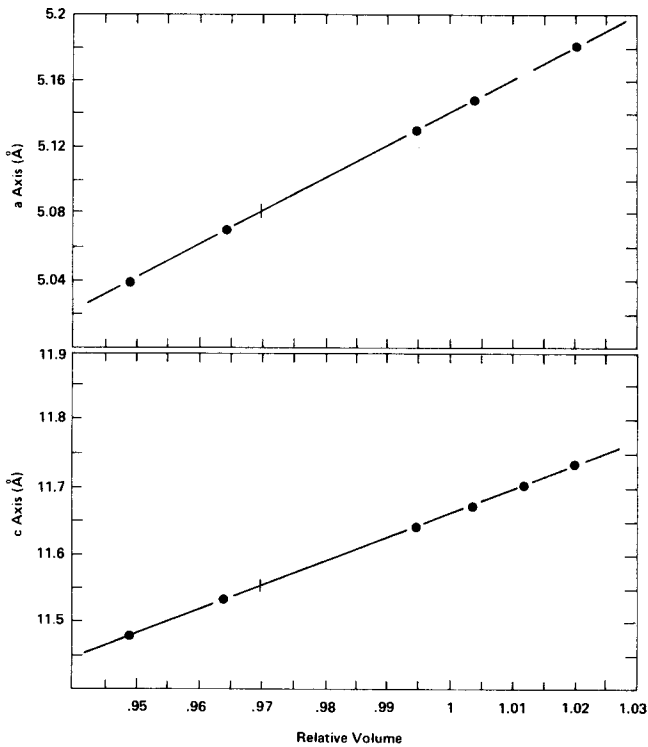


FIGURE 1 Unit cell parameters (Å) of tetragonal BiVO_4 at various temperatures and pressure versus reduced unit-cell volume.

the Bi^{3+} results in the ferroelastic distortion, whereas the V^{5+} tetrahedron plays a much smaller role (David *et al.*, 1979; Sleight *et al.*, 1979; David and Wood, 1983). The transition to the low-symmetry phase results in only a small movement of the oxygen and vanadium ions; however, the local symmetry of the VO_4 tetrahedron is reduced.

Bond lengths and corresponding bond strengths for the oxygen polyhedra surrounding the Bi and V ions are listed in Table IV. Bond strengths were calculated from bond lengths with the expression derived by Brown (1978):

$$s = (R/R_0)^{-N},$$

where s is bond strength, R is bond length, and R_0 and N are constants. Empirical values for R_0 and N from Brown and Wu (1976) were used

TABLE III

Selected interatomic distances and angles for tetragonal BiVO_4 at 1.6 and 4.3 GPa

Parameter		1.6 GPa	4.3 GPa
<i>V tetrahedron</i>	V-O [4]	1.724(14)	1.724(15)
	O-O [4]	2.75(2)	2.75(2)
	O-O [2]	2.93(3)	2.93(3)
	O-T-O [4]	105.9(4)	106.1(4)
	O-T-O [2]	116.9(8)	116.5(8)
	Volume (\AA^3)	2.60	2.60
<i>Bi polyhedron</i>	Bi-O [4]	2.405(14)	2.393(13)
	Bi-O [4]	2.472(12)	2.445(12)
	O-O [4]	2.78(1)	2.75(1)
	O-O [4]	2.98(3)	2.95(3)
	O-O [4]	3.00(1)	2.98(1)
	O-O [2]	2.93(3)	2.91(2)
	O-Bi-O [4]	69.4(3)	69.3(3)
	O-Bi-O [4]	75.4(5)	75.2(5)
	O-Bi-O [4]	75.9(3)	75.9(3)
	O-Bi-O [2]	72.6(7)	73.0(6)
	Volume (\AA^3)	25.7	25.2

TABLE IV

Bond lengths and bond strengths for BiVO_4 at 1.6 and 4.3 GPa

Pressure	Bond type	Length (\AA)	Strength Σs	Ideal Σs	
16 kbar	Bi-O	2.41(1)	0.4081(11)	0.764	0.75
	Bi-O	2.47(1)	0.3561(9)		
	V-O	1.72(1)	1.214(47)	1.287	1.25
	V-O	2.99(1)	0.073(2)		
40 kbar	Bi-O	2.39(1)	0.418(12)	0.793	0.75
	Bi-O	2.45(1)	0.375(8)		
	V-O	1.72(1)	1.215(47)	1.291	1.25
	V-O	2.95(1)	0.0762(2)		

Estimated valence

	16 kbar	40 kbar	Formal valence
Σs (to Bi)	3.05(1)	3.17(1)	3
Σs (to V)	5.15(20)	5.17(20)	5
Σs (to O)	2.05(4)	2.08(4)	2

in these calculations. Calculated bond strengths are similar to formal valences in all cases. Calculated values are slightly larger, however, and this discrepancy is greater for the higher-pressure data. David (1981), on the other hand, found that bond strengths in BiVO_4 at high temperatures were *smaller* than the formal valences. This effect can be explained by the fact that the parameters used in deriving the bond strengths were obtained from crystals at ambient conditions. With increasing temperature the bond strengths decrease and the bond lengths increase, so that the calculated bond strengths at high temperature can be expected to sum to less than their formal valences. In an analogous manner, increased pressure increases the bond strength and reduces the bond length, which results in the derived bond strengths with ambient parameters to sum to more than formal valences.

Comparison with other scheelite-type compounds

Hazen *et al.* (1984) determined the high-pressure structural response of five scheelite-type tungstates and molybdates, including CaWO_4 , CaMoO_4 , PbWO_4 , PbMoO_4 , and CdMoO_4 . All of these ABO_4 compounds displayed similar high-pressure behavior. The B^{6+} tetrahedron remained constant in size and shape at all pressures studied to 6.0 GPa, whereas the 8-coordinated A^{2+} polyhedron underwent significant compression. In all of these compounds, furthermore, the tetragonal c axis was significantly more compressible than a because of anisotropic compression of the large 8-coordinated site.

The same changes are displayed by BiVO_4 between 1.6 and 4.3 GPa. Bismuth vanadate compression is anisotropic, with c -axis compression (0.003 GPa^{-1}) approximately 1.5 times that of the a axis (0.002 GPa^{-1}). Tetrahedral compressibility is negligible, whereas the bismuth 8-coordinated site undergoes significant compression between 1.6 and 4.3 GPa.

In spite of the structural similarities of different scheelite-type compounds, the magnitudes of compression differ widely among these ABO_4 compounds. The bulk modulus of tetragonal BiVO_4 (approximately 150 GPa) is significantly greater than that of the tungstates and molybdates (70 to 100 GPa). This difference is a result of the greater compressibility of divalent cation polyhedra (Ca^{2+} , Pb^{2+} , and Cd^{2+}) in the tungstates and molybdates, compared to the compressibility of the Bi^{3+} polyhedron. It is observed that bulk moduli

of these scheelite-type compounds are primarily a function of 8-coordinated site valence. It is predicted, therefore, that alkali scheelites such as NaReO_4 and KRuO_4 will have the greatest compressibilities because of the relatively weak K–O and Na–O bonds. Compounds of the type $A^{2+}B^{6+}O_4$, such as the tungstates and molybdates, will be somewhat less compressible. Scheelites with compositions $A^{3+}B^{5+}O_4$ will be even less compressible, and those of the type $A^{4+}B^{4+}O_4$, including ZrGeO_4 and possible high-pressure forms of silicates, are predicted to be relatively incompressible because of the rigid A–O bonds. Note that in all of these scheelite-type compounds the tetrahedral B–O bonds will undergo little if any change with pressure; it is the response of A–O bonds that governs the phase transitions and equations-of-state properties in these compounds.

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