iopscience.iop.org

Equation of state of scheelite-structured $ZrGeO_4$ and $HfGeO_4$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 8241

(http://iopscience.iop.org/0953-8984/18/35/011)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 28/05/2010 at 13:26

Please note that terms and conditions apply.

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **18** (2006) 8241–8250 doi:10.1088/0953-8984/18/35/011

Equation of state of scheelite-structured $ZrGeO_4$ and $HfGeO_4$

Vinod Panchal[1], **Nandini Garg**[1], **S N Achary**[2], **A K Tyagi**[2] **and Surinder M Sharma**[1,3]

[1] Synchrotron Radiation Section, Bhabha Atomic Research Centre, Mumbai 400 085, India
[2] Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

E-mail: smsharma@magnum.barc.ernet.in

Received 10 May 2006, in final form 19 July 2006
Published 15 August 2006
Online at stacks.iop.org/JPhysCM/18/8241

Abstract
The high-pressure behaviour of scheelite-structured $ZrGeO_4$ and $HfGeO_4$ has been investigated with the help of angle-dispersive powder x-ray diffraction measurements. Our results show that these compounds do not undergo any phase transition up to the pressures of 20.7 and 19.0 GPa, respectively. The isothermal bulk modulus and its pressure derivatives are found to be 238 GPa and 4.5 for $ZrGeO_4$, and 242 GPa and 4.8 for $HfGeO_4$, implying that these germanates are highly incompressible.

1. Introduction

The ABO_4-type scheelite-structured compounds have important applications as ceramic pigments, laser materials when doped with some impurity atoms, and as high-density x-ray phosphors in radiographic imaging [1–3]. As several scheelite-structured silicates and germanates of hafnium, zirconium, uranium and thorium are found in the earth's crust, the understanding of high-pressure behaviour of these have important geophysical implications. Several high-pressure investigations on scheelite molybdates and tungstates have shown that the scheelite-structured compounds transform to lower symmetry monoclinic structures under high pressures. For example, $BaWO_4$, $BaMoO_4$, and $CaWO_4$ transform to monoclinic fergusonite phase while calcium tungstate eventually becomes amorphous at ~40 GPa [4–7]. Likewise, strontium tungstate, after going through the symmetry lowering phase changes, decomposes irreversibly at high pressures into its constituent oxides [8]. At high temperatures and pressures, scheelite-structured lithium gadolinium fluoride also undergoes phase transitions and eventual decomposition [9]. In contrast, under similar conditions of high pressures and high temperatures, the silicates of hafnium and zirconium are known to directly decompose into the constituent oxides [10]. However, at ambient temperatures the decomposition is found to be suppressed. For example, scheelite $ZrSiO_4$ does not undergo any phase transition or

---

[3] Author to whom any correspondence should be addressed.

decomposition even up to ~52.5 GPa [11]. We should also mention here that due to its large bulk modulus (>300 GPa), this compound has been claimed to be the hardest tetrahedrally bonded silicate.

It is well known that materials which have networks of tetrahedra comprising strong covalent bonds fall in the category of materials that are quite incompressible [12]. The scheelite-structured ABO_4 compounds can be formed through several valence combinations of the A and B cations (e.g., 1,7; 2,6; 3,5 and 4,4 for A and B respectively) and it has been observed that there is an increase in the degree of covalency and decrease in the ionicity when the A, B valencies vary from 1,7 to 4,4 [13]. This implies that 4,4 compounds would be more incompressible than other scheelite compounds. To gain a further understanding of this set of compounds, it would be useful to undertake high-pressure investigations of transition metal germanates (4,4 compounds). Therefore, we have carried out high-pressure studies on isostructural $HfGeO_4$ and $ZrGeO_4$.

2. Experimental details

Scheelite-structured $ZrGeO_4$ and $HfGeO_4$ were synthesized using the conventional ceramic route. For this the appropriate amounts of HfO_2/ZrO_2 (99.0% pure, IRE Ltd, India) and GeO_2 (99.99% pure, Alpha Aesar) were heated in a pellet form at 1200 °C for 48 h, with intermittent grinding and pelletization. To ensure the absence of any traces of moisture in the starting materials, these were heated at 1000 °C for ~24 h. The $HfGeO_4$ and $ZrGeO_4$ thus formed were characterized with the help of x-ray diffraction measurements. Recorded x-ray diffraction profiles show the existence of remnant oxide impurities along with the scheelite-structured germanates. Detailed analyses of our diffraction patterns show that the fractional abundances of various components are $ZrGeO_4$:GeO_2:ZrO_2::92:4:4 and $HfGeO_4$:HfO_2::95:5. At ambient conditions, the lattice parameters of these compounds are determined to be $a = 4.8700 \pm 0.0001$ Å, $c = 10.5400 \pm 0.0005$ Å for $ZrGeO_4$ and $a = 4.8600 \pm 0.0002$ Å, $c = 10.4900 \pm 0.0006$ Å for $HfGeO_4$. These match well with the cell parameters recorded earlier for these compounds, namely $a = 4.866(2)$ Å, $c = 10.550(2)$ Å for $ZrGeO_4$ [14] and $a = 4.862(1)$ Å, $c = 10.497(2)$ Å for $HfGeO_4$ [15]. However, the estimated standard deviations mentioned above represent the precision of the fits and do not take into account the probable errors due to other factors such as the finite pixel size of the imaging plate and the consequent error in the estimation of distance between the sample and imaging plate. If these sources of error are also taken into account, the estimated standard deviations for the cell constants are larger. For example, then $a = 4.87 \pm 0.01$ Å, $c = 10.54 \pm 0.02$ Å for $ZrGeO_4$ and $a = 4.86 \pm 0.01$ Å, $c = 10.49 \pm 0.02$ Å for $HfGeO_4$.

In different experimental runs, finely ground powder samples of zirconium germanate and hafnium germanate, along with a few particles of gold (pressure marker), were loaded in a hole of ~140 μm diameter of a pre-indented (~60 μm) tungsten gasket mounted in a Mao–Bell type of diamond anvil cell. For these experiments, a 4:1 methanol–ethanol mixture was used as a pressure-transmitting medium. Angle-dispersive x-ray diffraction measurements were carried out at the XRD1 beamline at the Elettra synchrotron source using monochromatic x-rays of wavelength 0.6726 Å, (calibrated with a LaB_6 NIST standard). The x-rays were collimated to ~100 μm and the two-dimensional diffraction rings, collected on a MAR 345 imaging plate, were converted to one-dimensional diffraction profiles using FIT2D software [16]. Refinement of the lattice parameters was carried out using Le Bail fits as incorporated in the GSAS software [17]. The pressure on the sample was deduced using the standard equation of state of gold [18]. The experimental data were recorded up to ~20.7 GPa for $ZrGeO_4$ and 19 GPa for $HfGeO_4$.

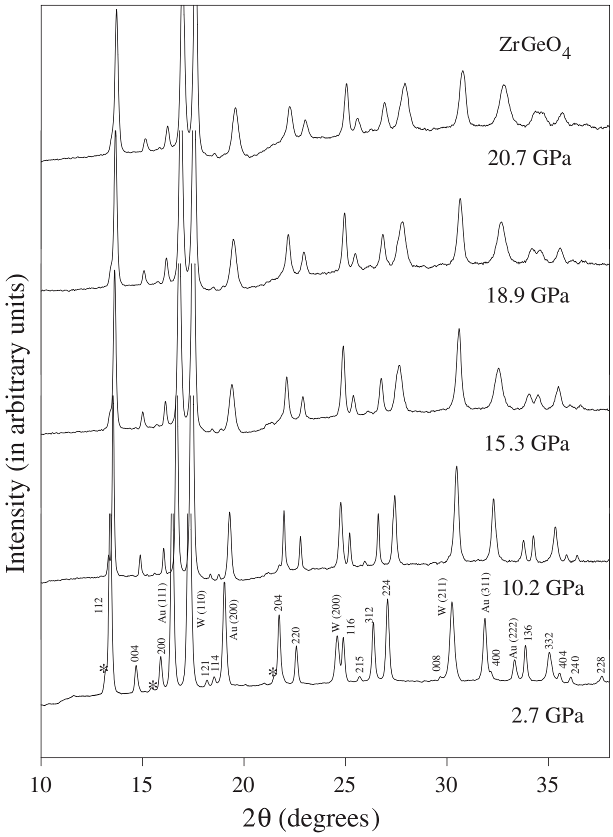

Figure 1. X-ray powder diffraction patterns of scheelite $ZrGeO_4$ at various pressures. Au (hkl) and W (hkl) represent the diffraction peaks from gold and tungsten, respectively. The asteriks indicate the diffraction peaks from ZrO_2 and GeO_2.

3. Results and discussion

The x-ray diffraction profiles of $ZrGeO_4$ and $HfGeO_4$ at a few representative pressures are shown in figures 1 and 2, respectively. In these, Au (hkl) and W (hkl) represent the diffraction peaks corresponding to gold and tungsten, respectively. The weak diffraction peaks marked with asterisks are identified to be due to the oxide impurities, such as ZrO_2, GeO_2 and HfO_2.[4] The observed pressure-induced variations in the diffraction patterns show that both these compounds do not undergo any phase transition or discernible decomposition up to ~20 GPa. The FWHM of the gold diffraction peak indicates that, in these measurements, the pressure was hydrostatic up to pressures of ~10 GPa and quasi-hydrostatic beyond this.

The variations of the lattice parameters a and c with pressure are given in figures 3(a) and that of the c/a ratio in figure 3(b) for $ZrGeO_4$. The corresponding variations for $HfGeO_4$ are given in figures 4(a) and (b), respectively. The axial compressibilities ($\frac{1}{l}\frac{\mathrm{d}l}{\mathrm{d}P}$) for the cell constants a and c have been calculated for both these compounds and are given in table 1. These results show that the compression is anisotropic, the c-axis being almost 1.5 and 1.3 times more compressible than the a-axis for $ZrGeO_4$ and $HfGeO_4$, respectively. These anisotropies in the

---

[4] It may be noted that these weak diffraction peaks are the strongest peaks of the unreacted oxides.

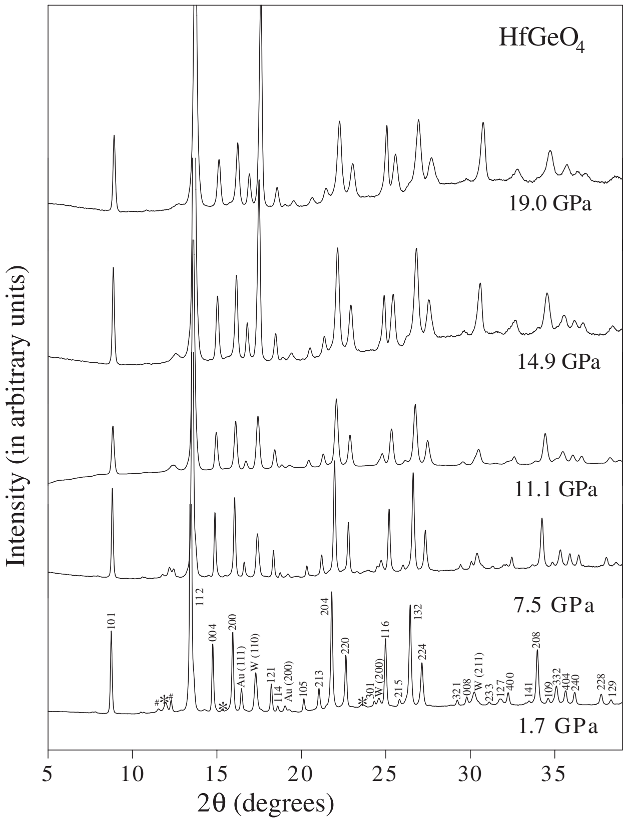

Figure 2. X-ray powder diffraction patterns of scheelite HfGeO$_4$ at various pressures. Au (*hkl*) and W (*hkl*) represent the diffraction peaks from gold and tungsten, respectively. The asteriks indicate the diffraction peaks from HfO$_2$ and the # represents the diffraction peaks from some unknown impurity.

Table 1. The linear compressibility along the *a* and *c* axes.

Compound	$1/a_0\ \mathrm{d}a/\mathrm{d}P$ (GPa^{-1})	$1/c_0\ \mathrm{d}c/\mathrm{d}P$ (GPa^{-1})	Ratio of axial compressibilities
ZrGeO$_4$	10.11×10^{-4}	1.49×10^{-3}	1.47
HfGeO$_4$	10.42×10^{-4}	1.39×10^{-3}	1.33

axial compressibility are comparable to that observed for ZrSiO$_4$ (~1.5) by Scott *et al* [11] and are also similar to other scheelite compounds [4, 5, 19].

The equations of state for ZrGeO$_4$ and HfGeO$_4$ are plotted in figures 5 and 6, respectively. The isothermal bulk modulus K_0 and its pressure derivative K_0' are determined by fitting the P–V data to the Birch–Murnaghan equation of state [20] and are found to be $K_0 = 238 \pm 1.6$ GPa, $K_0' = 4.5 \pm 0.2$ for ZrGeO$_4$ and $K_0 = 242 \pm 1.2$ GPa, $K_0' = 4.8 \pm 0.2$ for HfGeO$_4$. Even if we fit the data corresponding only to the hydrostatic conditions (~10 GPa), the bulk moduli are comparable, namely $K_0 = 240$ GPa $K_0' = 3.4$ and $K_0 = 244$ GPa, $K_0' = 4.2$ for ZrGeO$_4$ and HfGeO$_4$, respectively.

To rationalize these results in the context of other scheelite-structured compounds, we refer to the empirical models which have been developed for predicting the bulk moduli of

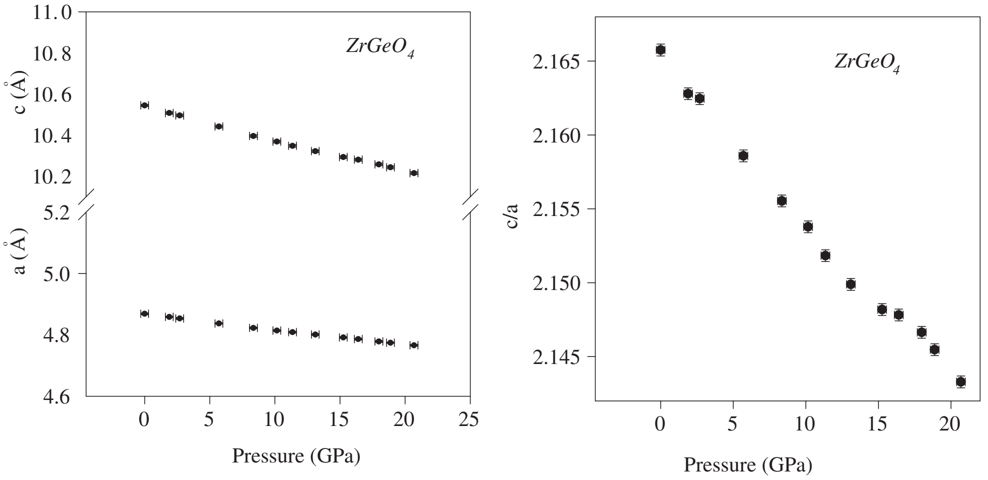

Figure 3. Pressure dependence of (a) lattice parameters and (b) c/a ratio for the scheelite phase of $ZrGeO_4$.

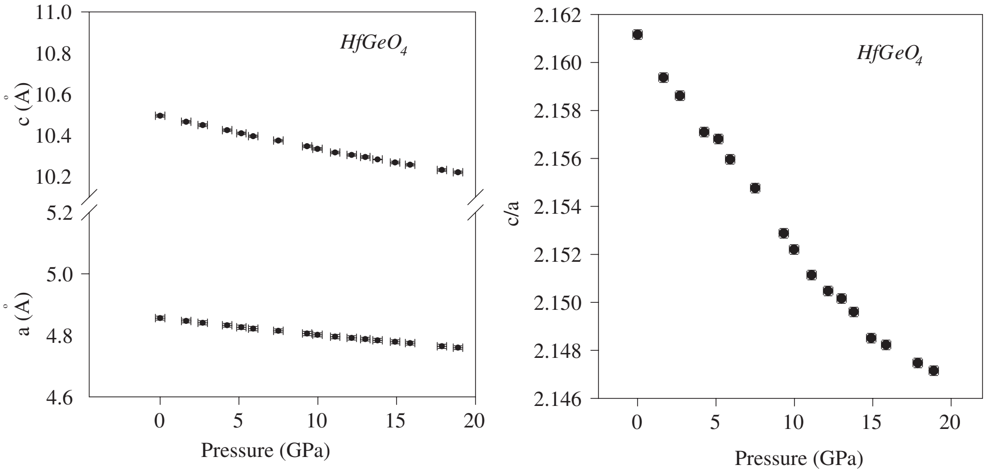

Figure 4. Pressure dependence of (a) lattice parameters and (b) c/a ratio for the scheelite phase of $HfGeO_4$.

these compounds [13, 19, 21, 22]. Two of these [13, 19] exploit the empirical observation that the bulk modulus is related to the cation charge density of the polyhedra. In particular, Hazen *et al* [13] observed that for certain oxides and silicates, the bulk modulus is related essentially to the compressibility of the A cation polyhedra, as the B cation tetrahedra behave like rigid units under pressure. And for these compounds, the polyhedral compressibility is proportional to the polyhedral volume divided by the formal cationic charge. For the compounds analysed by Hazen *et al* [23], one finds that K_0 (in GPa) is $750Z_i/d^3$, where Z_i is the cationic formal charge and d is the mean cation–O distance (in Å). Errandonea *et al* [19] fitted the experimentally determined bulk moduli of several scheelite-structured compounds as a function of the A cationic charge per unit volume of the AO_8 polyhedra and found that these

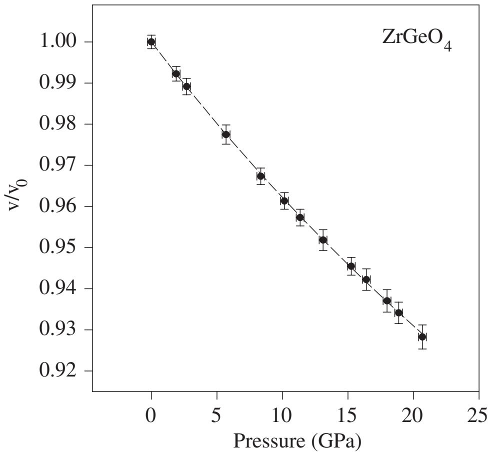

Figure 5. Pressure dependence of V/V_0 for the scheelite phase of ZrGeO$_4$. The dashed line shows the fit to the Birch–Murnaghan equation of state.

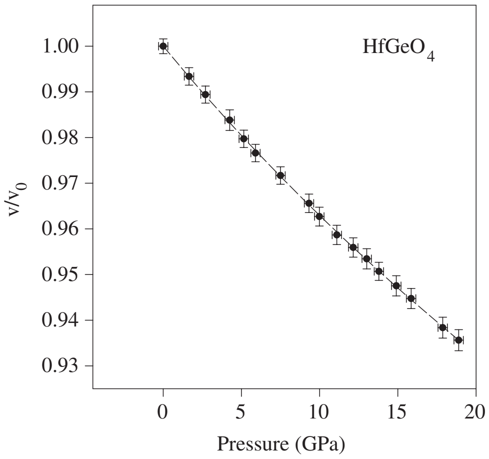

Figure 6. Pressure dependence of V/V_0 for the scheelite phase of HfGeO$_4$. The dashed line shows the fit to the Birch–Murnaghan equation of state.

had a linear relationship, namely

$$K_0\ (\mathrm{GPa}) = 610 Z_i/d^3. \tag{1}$$

Here again d is the mean cation–O distance (in Å). The difference in the prefactors given above [19, 23] arises because of the fact that Errandonea *et al* have included only those compounds which have scheelite or scheelite-like structures, unlike Hazen *et al* [23], who had included 38 oxides and silicates having various (non-scheelite) structures (NaCl-type, CsCl-type, corundum-type, rutile-like, quartz-like, spinel-type, garnet-like, fluorite-like, zircon-type, CdI$_2$-type, zincite-type, boron nitride, diamond, graphite, etc). In view of this, the fit given by Errandonea *et al* [19] is more appropriate for the compounds presented here. We will term this as model I.

Ming *et al* [24] have shown that the bulk moduli can be related to the ambient pressure molar volumes. Using this correlation and the formulation of Cohen for the diamond-like semiconductors [21], Scott *et al* [11] have proposed a semi-theoretical relationship for the scheelite-structured compounds. We shall term this relationship between K_0 and V_0, given below, as model II.

$$K_0\ (\text{GPa}) = (Y - Z\lambda)(V_0)^n \tag{2}$$

where λ is the Cohen polarization factor, the value of which varies between 0 and 3 as determined by one-half of the difference in valency between the A and B cations, and Y, Z and n are the parameters to be obtained by fitting the known experimental values of bulk moduli of different scheelite compounds and V_0 is the molar volume (cm^3 mol^{-1}). Scott *et al* [11] obtained their fitted parameters by including scheelite $ZrSiO_4$, and these are $Y = 2.02 \pm 0.06 \times 10^5$ and $Z = 5.2 \pm 0.4 \times 10^4$, $n = -1.84$. The essential difference between this model and that proposed by [12] and [18] is that here the contributions from the covalent bonds are also considered, as discussed by Cohen [21].

In addition to the empirical relations mentioned above, Westrenen *et al* [22] have proposed that the bulk modulus K_0 varies as a function of the molar volume V_0 (in cm^3 mol^{-1}) and the product of the formal charges on the A and B cations ($z_A z_B$). They obtained the following relationship (model III) by fitting the experimental data of several ABO_4 compounds, such as $ZrSiO_4$ (cubic as well as scheelite) and other scheelite-structured compounds.

$$K_0\ (\text{GPa}) = A^*[V_0/(z_A z_B)]^m \tag{3}$$

where $A = 886 \pm 30$, $m = -1.67 \pm 0.03$.

Using these models, we can predict the bulk moduli for $ZrGeO_4$ and $HfGeO_4$, and these are $K_0 = 228$ and 231 GPa (model I), 257 and 262 GPa (model II), and 212 and 215 GPa (model III), respectively. Therefore, for the two germanates presented here, the predicted bulk moduli from these empirical models are reasonably close to our measured values.

However, to effectively evaluate the relative predictive capability of the three models, one must fit these to the same data set. Therefore, we have refitted the data given in [19] to all these models. The comparison of the observed and the fitted bulk moduli in all the three models is given in table 2. ($K1$ is as given by the original fits of the respective authors and $K2$ is after our refitting). The results show that now all the three models predict the bulk moduli of scheelite-structured compounds with a better accuracy, except that for models II and III, significant deviations still exist for the vanadates. We should also mention here that, in general, the deviations from the fits are probably not related to the value of K' used in the determination of the equation of state (column 4 in table 2). For scheelite $ZrSiO_4$ the observed bulk modulus is consistently off from the predictions of all the models. Also its value exceeds the bulk modulus of the zircon structure by ~30% (despite the fact that K' in both cases is 4). In fact, due to this reason and also because its bulk modulus is much higher than predicted by first principles calculations [25], doubts have been raised about the measured value of the bulk modulus [19]. Because of this, we excluded scheelite $ZrSiO_4$ from the new fits.

Our results presented here show that (4,4) germanate scheelites are highly incompressible materials like the corresponding silicate scheelites. In fact, these are the most incompressible scheelite germanates studied so far, as only octahedrally coordinated argutite has a higher bulk modulus [26, 27]. Therefore the behaviour of these compounds is very similar to that of $ZrSiO_4$.

4. Conclusions

Our high-pressure x-ray diffraction studies on scheelite zirconium and hafnium germanates show that these compounds do not undergo any phase transition or decomposition up to ~20 GPa. In addition, the favourable comparison between the large bulk moduli of these

Table 2. Comparison of observed and computed bulk moduli of scheelite and scheelite-like structures from the three models discussed in the text. The included structures basically fall in three space groups, namely $I4_1/a$ (tetragonal, scheelite), $Pnma$ (orthorhombic, pseudo-scheelite) and $I4_1/amd$ (tetragonal, zircon-like). The bulk moduli calculated with the earlier and the modified fits are represented by $K1$ and $K2$ respectively. The parameters of the new fits to model II and model III are $Y = 1.84 \times 10^5$, $Z = 3.84 \times 10^4$, $n = -1.84$ (equation (2)) and $A = 1199.977$, $m = -1.91$ (equation (3)). ΔK shows the difference between the experimental bulk moduli and the calculated ones using the new parameters.

Compounds	Space group	Experimental bulk moduli (K)	Experimental (K')	References	Calculated bulk moduli (Model I) ($K1$)	$K - K1 = \Delta K$	Calculated bulk moduli (Model II) ($K2$)	Calculated bulk moduli (Model II) ($K1$)	$K - K2 = \Delta K$	Calculated bulk moduli (Model III) ($K2$)	Calculated bulk moduli (Model III) ($K1$)	$K - K2 = \Delta K$
$ZrSiO_4$	$I4_1/a$	301	4	[11]	229.9	71.1	268.3	238.1	32.7	271.3	241.9	29.7
$ZrSiO_4$	$I4_1/amd$	215	4	[23]	216.2	−1.2	215.0	297.1	0.0	215.5	197.9	−0.5
$ZrGeO_4$	$I4_1/a$	238	3.4	This work	228.20	9.8	232.3	257.3	5.7	233.6	212.3	4.4
$HfGeO_4$	$I4_1/a$	242	4.2	This work	231.4	10.6	236.7	262.2	5.3	238.2	215.9	3.8
$LaNbO_4$	$I4_1/a$	111		[19]	116.4	−5.4	108.5	108.5	2.5	119.4	118.2	−8.4
YVO_4	$I4_1/a$	138	4.6	[19]	136.1	1.9	144.9	144.9	−6.9	161.4	153.7	−23.4
$TbVO_4$	$I4_1/amd$	149		[19]	137.6	11.4	112.8	112.8	36.2	124.3	122.4	24.7
$BiVO_4$	$I4_1/a$	150		[19]	141.0	9.0	127.5	127.5	22.5	141.3	136.9	8.7
$DyVO_4$	$I4_1/amd$	160		[19]	140.3	19.7	115.2	115.3	44.8	127.1	124.8	32.9
YVO_4	$I4_1/amd$	130	4.4	[19]	141.4	−11.4	118.2	118.2	11.8	130.5	127.7	−0.5
$ErVO_4$	$I4_1/amd$	136		[19]	142.6	−6.6	119.6	119.6	16.4	132.2	129.1	3.8
$LuPO_4$	$I4_1/amd$	166		[19]	149.2	16.8	154.6	154.6	11.4	172.6	162.9	−6.6
$BaSO_4$	$Pnma$	58		[19]	51.1	6.9	74.4	69.4	−16.4	72.4	76.4	−14.4
$BaWO_4$	$I4_1/a$	57	3.5	[4]	63.5	−6.5	55.9	52.1	1.1	53.8	58.9	3.2
$BaMoO_4$	$I4_1/a$	56	4	[6]	59.9	−3.9	57.9	54.1	−1.9	59.7	60.9	−3.7
$PbWO_4$	$I4_1/a$	64	4	[13]	71.1	−7.1	69.4	64.8	−5.4	67.4	71.8	−3.4
		69	4.5	[29]		−2.1			−0.4			1.6
$PbMoO_4$	$I4_1/a$	64	4	[13]	71.4	−7.4	69.9	65.3	−5.9	67.9	72.2	−3.9
		71	5.6	[29]		−0.4			1.1			3.1
$SrWO_4$	$I4_1/a$	63	5.2	[19]	72.9	−9.9	72.5	67.7	−9.5	70.6	74.7	−7.6
		66	8.13	[8]		−6.3			−6.5			−4.6

Table 2. (Continued.)

Compounds	Space group	Experimental bulk moduli (K)	Experimental (K')	References	Calculated bulk moduli (Model I) $(K1)$	$K - K1 = \Delta K$	Calculated bulk moduli (Model II) $(K2)$	Calculated bulk moduli (Model II) $(K1)$	$K - K2 = \Delta K$	Calculated bulk moduli (Model III) $(K2)$	Calculated bulk moduli (Model III) $(K1)$	$K - K2 = \Delta K$
$SrMoO_4$	$I4_1/a$	73		[19]	73.1	−0.1	73.0	68.1	0.0	71.0	75.1	2.0
$EuWO_4$	$I4_1/a$	65	4.7	[19]	72.9	−7.9	72.5	67.7	−7.5	70.5	74.7	−5.5
$NaY(WO_4)_2$	$I4_1/a$	77		[19]	80.2	−3.2	—	—	—	—	—	—
$CaMoO_4$	$I4_1/a$	82	4	[13]	82.2	−0.2,	90.1	84.1	−8.1	88.4	90.9	−6.4
		83	4.2	[29]		0.8			−7.1			−5.4
$CaWO_4$	$I4_1/a$	75	5.6	[19]	82.3	−7.3	89.8	83.9	−14.8	88.1	90.7	−13.1
$SrSO_4$	$Pnma$	82		[19]	82.8	−0.8	—	—	—	—	—	—
$CdMoO_4$	$I4_1/a$	104	4	[13]	86.2	17.8	98.2	91.6	5.8	96.7	98.3	7.3
$KReO_4$	$I4_1/a$	18		[19]	28.1	−10.1	34.9	34.9	−16.9	18.7	23.5	−0.7
$TIReO_4$	$Pnma$	26		[24]	28.9	−2.9	30.9	30.9	−4.9	16.5	20.9	9.5
$AgReO_4$	$I4_1/a$	31	4	[19]	37.9	−6.9	48.8	48.8	−17.8	26.5	31.7	4.5

compounds with that of scheelite $ZrSiO_4$ (computed from first principles [25]) implies that these scheelite germanates are as incompressible as the corresponding scheelite silicates. On reanalysis of the published data, we have shown that all the three empirical models proposed so far predict the bulk moduli of the scheelite-structured compounds reasonably well except for the vanadates.

References

[1] Eppler R A 1970 *J. Am. Ceram. Soc.* **73** 457
[2] Federvoskikh Y A, Shulgin B V, Emelchenko G A, Garilor F F and Ilyukhin V V 1973 *Inorg. Mater.* **9** 384
[3] Lambert P M 2000 *Mater. Res. Bull.* **35** 383
[4] Panchal V, Garg N, Chauhan A K, Sangeeta and Sharma S M 2004 *Solid State Commun.* **130** 203
[5] Grzechnik A, Crichton W A, Marshall W G and Friese K 2006 *J. Phys.: Condens. Matter* **18** 3017
[6] Panchal V, Garg N and Sharma S M 2006 *J. Phys.: Condens. Matter* **18** 3917
[7] Errandonea D, Somayazulu M and Häusermann D 2003 *Phys. Status Solidi* b **253** 162
[8] Grzechnik A, Crichton W A and Hanfland M 2005 *Phys. Status Solidi* b **242** 2795
[9] Grzechnik A, Crichton W A, Bourier P, Dmitriev V, Weber H P and Gesland J Y 2004 *J. Phys.: Condens. Matter* **16** 7779
[10] Liu L 1982 *Earth Planet. Sci. Lett.* **57** 110
[11] Scott H P, Williams Q and Knittle E 2002 *Phys. Rev. Lett.* **88** 015506
[12] Aleksandrov I, Goncharov A, Zisman A and Stishov S 1987 *Sov. Phys.—JETP* **66** 384
[13] Hazen R M, Finger L W and Mariathasan J W E 1985 *J. Phys. Chem. Solids* **46** 253
[14] Ennaciri A, Michelÿ D, Perez Y, Jorbaÿ M and Pannetierÿ J 1984 *Mater. Res. Bull.* **19** 793
[15] Ennaciri A, Kahnÿ A and Michelÿ D 1986 *J. Less-Common Met.* **124** 105
[16] Hammersely A P, Svensson S O, Hanfland M, Fitch A N and Hausermann D 1996 *High Pressure Res.* **14** 235
[17] Larson A C and von Dreele R B 2000 *GSAS: General Structure Analysis System* Los Alamos National Laboratory
[18] Dewaele A, Loubeyre P and Mezouar M 2004 *Phys. Rev.* B **70** 094112
[19] Errandonea D, Pellicer-Porres J, Manjon F J, Segura A, Ferrer-Roca Ch, Kumar R S, Tschauner O, Rodriguez-Hernandez P, Lopez-solano J, Radescu S, Mujica A, Munoz A and Aquilanti G 2005 *Phys. Rev.* B **72** 174106
[20] Birch F 1978 *J. Geophys. Res.* **83** 1257
[21] Cohen M L 1985 *Phys. Rev.* B **32** 7988
[22] Westrenen W V, Frank M R, Fei Y, Hanchar J M, Finch R J and Zha C S 2005 *J. Am. Ceram. Soc.* **88** 1345
[23] Hazen R M and Finger L W 1979 *J. Geophys. Res.* **84** 6723
[24] Ming L C, Jayaraman A, Shieh S R and Kim Y H 1995 *Phys. Rev.* B **51** 12100
[25] Farman I, Balan E, Pickard Ch J and Maury F 2003 *Am. Mineral.* **88** 1633
[26] Yamanaka T and Ogata K 1991 *J. Appl. Crystallogr.* **24** 111
[27] Hazen R M and Finger L W 1981 *J. Phys. Chem. Solids* **42** 143
[28] Crichton W A and Grzechnik A 2004 *Z. Kristallogr. NCS* **219** 337
[29] Panchal V, Garg N and Sharma S M 2006 to be published