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Pressure-induced phase transformations in HfO_2 to 50 GPa studied by Raman spectroscopy

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High-pressure Raman studies were carried out at room temperature on HfO_2 single-crystal samples up to 50 GPa in the diamond anvil cell, with a methanol-ethanol pressure medium. From the changes in the Raman spectral features and the pressure dependence $d\omega/dP$ of the Raman modes, three pressure-induced phase transitions were found to occur at 4.3±0.2 GPa, 12±0.5 GPa, and 28±2 GPa. The first two high-pressure phases are nonquenchable while the high-pressure phase after the 28 GPa transition is quenchable. The high-pressure phase after the 4.3-GPa transition has been determined as orthorhombic belonging to the space group *Pbcm*, from earlier high-pressure Raman and x-ray studies. The 12-GPa transition and the 28-GPa transition, newly found in this study, are believed to have the same structure as that of the high-pressure polymorphs of ZrO_2 that occur at nearly the same pressures. For these, other orthorhombic and tetragonal structures, respectively, are proposed from the close similarity in high-pressure Raman behavior between ZrO_2 and HfO_2. The almost identical molar volumes, structural correspondence, and high-pressure behavior of ZrO_2 and HfO_2 suggest that the bulk modulus K_0 of HfO_2 should be nearly the same as that of ZrO_2 ($K_0=182\pm20$ GPa). A value for K_0 of 185±20 GPa is suggested for HfO_2.

I. INTRODUCTION

Zirconia (ZrO_2) and hafnia (HfO_2) are well-known high-temperature ceramic materials, of which zirconia has received much attention because of its many interesting and useful applications. Both the oxides crystallize in the so-called baddeleyite (monoclinic $P2_1/c$) structure which transform to a tetragonal and then to the cubic fluorite structure at high temperature, $>1700\,^\circ C$, under ambient conditions. The cubic phase of ZrO_2 stabilized by additions of yttria is an important gem, as well as a refractory material.

Pressure-induced phase transitions have been reported in both of the oxides.[1-12] Early quenching experiments[3,4] from high-pressure–high-temperature fields (4–11 GPa and 20–1700 °C) indicated a transformation of the monoclinic (baddeleyite) phase to a supposedly orthorhombic phase,[3,4] but subsequent *in situ* x-ray-diffraction studies on ZrO_2 (Refs. 5 and 12) could not verify this. Instead, they reported the high-pressure phase to be tetragonal. Tentative *P-T* diagrams for both ZrO_2 and HfO_2 have been proposed[1,13] showing the monoclinic (baddeleyite), tetragonal, and a high-pressure orthorhombic ($P2_12_12_1$) phases. Liu[14] has reported yet another pressure-induced phase change from baddeleyite to the cotunnite-type structure (orthorhombic) in both ZrO_2 and HfO_2, based on an x-ray study of the quenched material, from high-pressure–high-temperature fields in the range of 8–30 GPa and 1000°C.

Arashi *et al.*[15] have recently reported pressure-induced phases for ZrO_2 based on an *in situ* high-pressure Raman and x-ray-diffraction study. We were motivated to study HfO_2 using high-pressure Raman spectroscopy, to explore if the high-pressure–induced phase transition sequence reported for ZrO_2 would also occur for HfO_2. Two very recent[16,17] high-pressure Raman studies on HfO_2 to 10 GPa are worth mentioning, one of which has located the monoclinic to the orthorhombic phase transition in HfO_2 near 4 GPa, in excellent agreement with our results. Our Raman studies on HfO_2, however, extended to 50 GPa and we believe that we have clear Raman evidence for two new phase transitions near 12 and 28 GPa, akin to that of ZrO_2. We have also studied the reversibility of these pressure-induced transitions in some detail. These results will be presented and discussed in this paper.

TABLE I. Observed Raman frequencies in the baddeleyite and in the high-pressure orthorhombic I phase and their pressure dependencies. $\gamma = K_0 \times 1/\omega(d\omega/dP)$; the Gruneisen parameter γ was calculated using K_0 approximated to 200 GPa (see discussions). s,m,vs,w,vw indicate the intensity of the Raman peak.

Monoclinic (baddeleyite)				Orthorhombic I	
Raman frequency (cm^{-1})	Mode assignment	$d\omega/dP$ (cm^{-1}/GPa)	γ	Raman frequency (4.3 GPa) (cm^{-1})	$d\omega/dP$ (cm^{-1}/GPa)
113 s	A_g	6	10.6	117 m	1
133 s	A_g+B_g	1.8	2.7	135 w	0.5
148 s	A_g	1.6	2.2	143 w	1
164 m	B_g	1.5	1.8	164 m	1
242 m	B_g	0.5	0.4	174 m	0.2
257 s	A_g	1	0.8	198 vs	0.2
324 m		5	3.0	221 w	1
337 m	B_g	2.5	1.5	319 w	1
383 s	A_g	3.5	1.8	333 w	4
399 s	B_g	3.5	1.8	352 w	4
496 vs	A_g	−1	−0.4	383 vs	2.5
520 m	B_g	−1	−0.4	435 m	3.5
551 w	B_g	4	1.5	464 m	3.5
577 m	A_g	3.5	1.2	477 m	1.5
640 m	B_g	5	1.5	519 m	2.5
671 m	A_g	3	0.9	587 s	3.5
733* vw				597 s	4
				641 s	4
				679 s	4

II. EXPERIMENTS AND RESULTS

Single-crystal samples of HfO_2 grown by Remeika of Bell Labs were available to us. The crystals were millimeter size and of excellent optical quality. Their morphology reflected well-defined habit faces, as described by Arashi.[17] For high-pressure Raman work, thin crystal plates of appropriate size were chosen, to fit into the gasket hole of the diamond anvil cell.

Pressure was generated using a gasketed Mao-Bell–type diamond cell. Typically, the gasket-hole size was 150 μm in diameter and 70–80 μm in thickness and the diamond flat 600 μm in diameter. A 4:1 mixture of methanol-ethanol was used as a pressure medium. The well-known ruby fluorescence technique was employed for pressure calibration.

Raman spectra were taken using a Spex Triplemate instrument, provided with an OMA-III diode array detector system. Spectra were also taken with a Spex (1403) scanning double monochromater Raman instrument, equipped with PMT for photon counting. Data were acquired in both cases using computerized data-acquisition systems. For exciting the Raman spectrum we employed the 476.2 nm line from a krypton laser and also the 488 nm line of the argon laser. The power levels were kept around 5–10 mW. All the spectra were recorded at room temperature on unoriented samples.

The Raman spectrum of the monoclinic (baddeleyite) phase is shown in Fig. 1 (bottom). Near 4.3 GPa the spectrum changes sharply, due to the pressure-induced phase transition from the monoclinic to the orthorhombic phase, as noted by Arashi.[17] The Raman spectrum of this phase recorded near 6 GPa is shown in Fig. 1 (top spectrum). In Table I are listed the observed Raman frequencies in the monoclinic phase and their pressure dependencies. The mode designation is after Arashi.[17] In the same table, the Raman frequencies observed in the orthorhombic high-pressure phase are listed. In Fig. 2 a sequence of Raman spectra are shown to demonstrate the evolution of the Raman spectral features, as pressure is increased and then released. This figure illustrates the

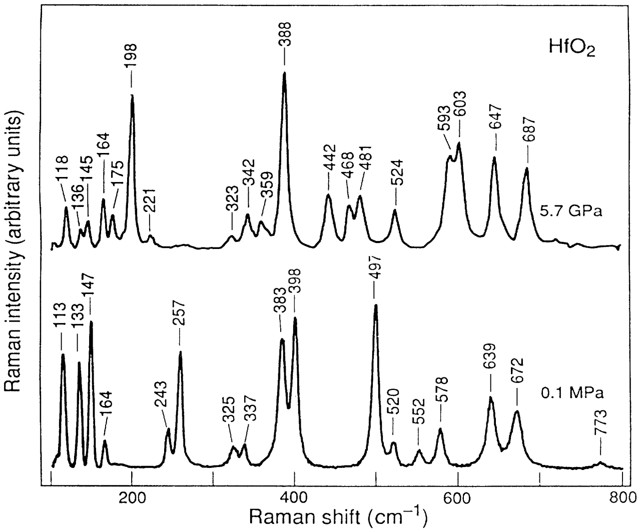

FIG. 1. The Raman spectrum of HfO_2, monoclinic (baddeleyite) phase at ambient pressure (bottom) and the high-pressure orthorhombic I (*Pbcm*) phase at 5.7 GPa recorded with the Spex Raman Double Monochromater.

ready reversibility of the monoclinic to orthorhombic phase transition. To be noted in this connection is the reversal of the spectrum at 3.9 GPa on the decreasing pressure cycle, due to the back transformation from orthorhombic to the low-pressure monoclinic phase. In the increasing pressure cycle the monoclinic to the orthorhombic transition occurs at 4.3 ± 0.2 GPa. Therefore, the hysteresis is less than 2 or 3 kbars at the most.

In Fig. 3 are shown a series of Raman spectra recorded at ambient pressure to 51.3 GPa, the highest pressure reached in this study. The spectra are a composite of two different experiments. In one series the spectra were recorded with the scanning Raman double monochromater, and in the other experiment with the Triplemate equipped with the OMA-III diode array detector. The spectral resolution in the latter is smaller and this shows up in the spectra. Also, there is the problem associated with the broadening of the Raman peaks at higher pressure due to the nonhydrostaticity of the pressure medium. Nevertheless, one can easily recognize the changes in the spectral features, which are presumably due to phase transitions. From the spectra recorded at 29.5 GPa it is quite clear that there is a definite change in the spectral features, which we believe is due to another phase transition near 28 ± 2 GPa. From the series of spectra recorded on the decreasing pressure cycle and shown in Fig. 4, it is quite clear that this high-pressure phase, the phase formed above 28 GPa, is quenchable to ambient pressure. In one experiment, we pressurized the sample to 25 GPa only and then released pressure, recording the Raman spectra on both the increasing and decreasing pressure cycle. This revealed that the sample pressurized to 25 GPa perfectly reversed to the monoclinic phase.

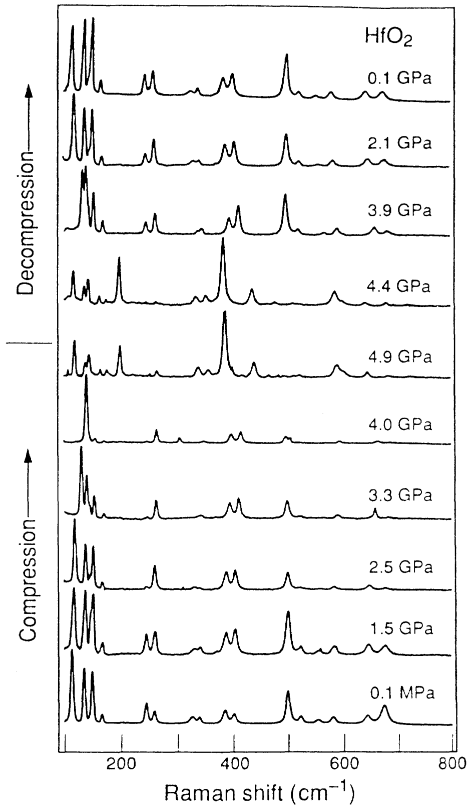

FIG. 2. Raman spectra of HfO_2 at different pressures, recorded with the Spex Raman Double Monochromater, during the pressure increasing and pressure decreasing cycle. The spectrum recorded at 4.9 GPa belongs to the orthorhombic I phase. On releasing pressure the spectrum reverses to the original monoclinic phase at 4 GPa.

In Figs. 5 and 6 the pressure dependence of the Raman peak frequencies is shown. Figure 5 shows the overall behavior up to 50 GPa, while Fig. 6 is an expanded version covering the range 0–25 GPa, to reveal some of the details. In particular, the transition near 12 GPa is clearly seen in this figure. Changes and abrupt shifts in the Raman peaks occur in three places due to pressure-induced phase transitions. These are marked by dashed lines in the figures. The corresponding transition pressures are 4.3 ± 0.2 GPa, 12 ± 0.5 GPa, and 28 ± 2 GPa.

The samples in the diamond cell were viewed under an optical microscope during pressurization. At the 4.3-GPa transition, dark bands rapidly moved across the

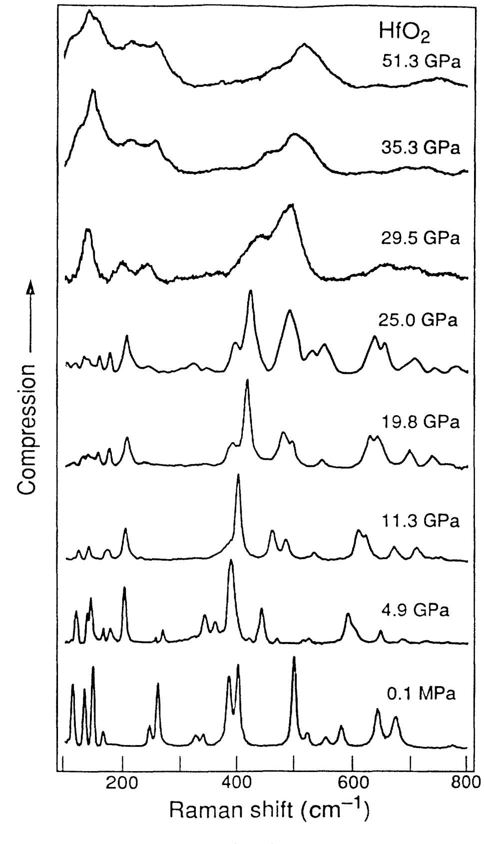

FIG. 3. Raman spectra of HfO_2 recorded at different pressures up to 51.3 GPa, the highest pressure reached in this study. The top three spectra were recorded with the Triplemate equipped with an OMA-III system, while the rest of the spectra were recorded with the Spex Raman Double Monochromater. Note the changes in the spectra recorded at 4.9, 19.8, and 29.5 GPa. These changes are attributed to three pressure-induced phase transitions.

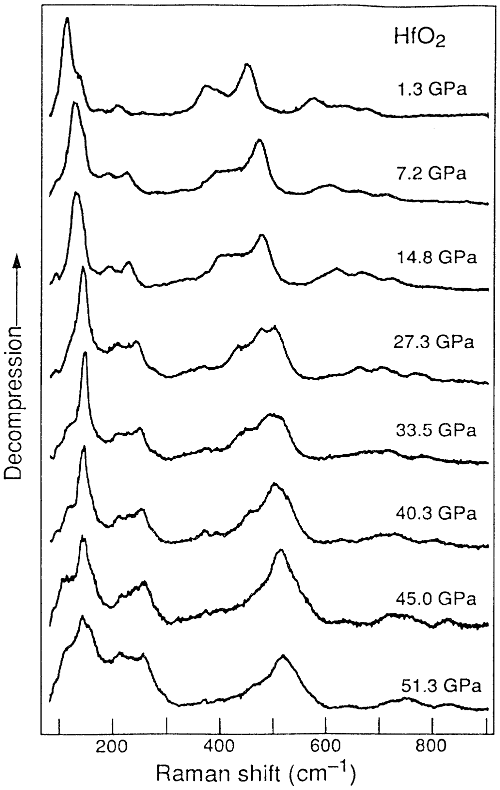

FIG. 4. Spectra recorded with the Triplemate instrument, on the pressure release cycle from 51.3 GPa. The spectral features remain more or less the same down to ambient pressure, indicating the quenchability of the highest-pressure phase.

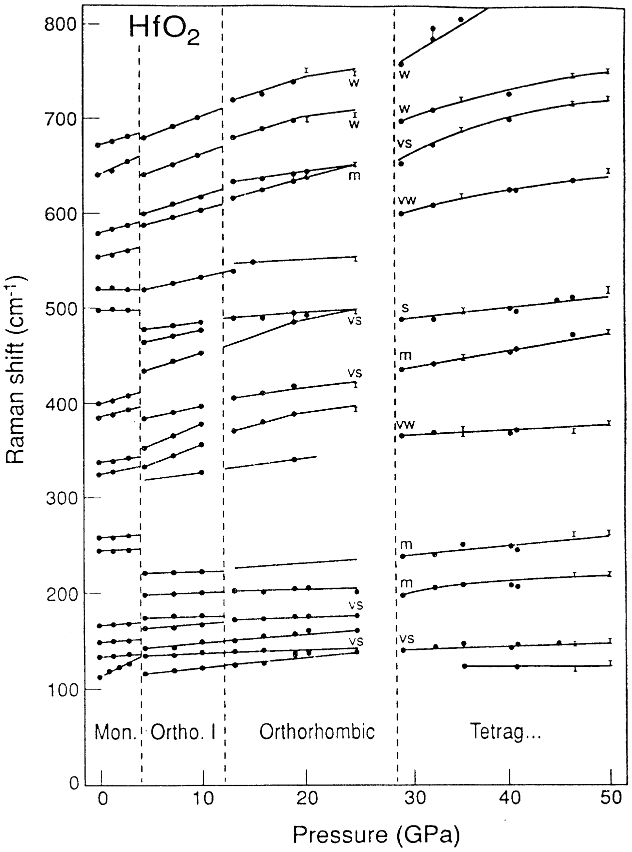

FIG. 5. Pressure dependence of the Raman peaks of HfO_2 to 51 GPa. The small letters vw, w, m, s, and vs indicate the intensity of the Raman peak, vw = very weak, w = weak, m = medium, s = strong, and vs = very strong. The dashed vertical lines mark the phase transition pressures; monoclinic to orthorhombic I to orthorhombic (?) and to tetragonal.

crystal plate and cleared. The dimensional changes if any were not observable. Close to the highest-pressure end the sample acquired a light yellow color.

III. DISCUSSION

In view of the close structural similarities that exist between ZrO_2 and HfO_2 a brief discussion of the pressure-induced phase transitions in ZrO_2 would be relevant to an understanding of the high-pressure behavior of HfO_2. There have been two types of investigations to unravel the complex P-T behavior of ZrO_2, namely, *in situ* x-ray-diffraction and Raman studies at high pressure on the one hand, and similar studies on quenched samples, from high-pressure–high-temperature fields. Consequently, a certain amount of confusion regarding the structure of the high-pressure phases exists, for quenching experiments and *in situ* studies have not always yielded the same result. Also, there seems to be a difference in behavior between pressurizing finely powdered material and single-crystal samples. Further, there are inconsistencies between the *in situ* x-ray-diffraction and Raman studies themselves. For instance, Ming and Manghnani[5] and Block, da Jornada, and Piermarini[12] have proposed a tetragonal phase for the 3.5-GPa transition, from *in situ* x-ray-diffraction studies. Alzyab, Perry, and Ingel[18] from their Raman studies have supported this. As opposed to these there are *in situ* Raman studies and x-ray studies[19,20] which have identified the 3.5-GPa phase transition in pure ZrO_2 as monoclinic to orthorhombic, in the space group *Pbcm*.

The high-pressure–high-temperature quenching experiments[14] have shown a transformation of the monoclinic (baddeleyite) phase to the so-called cotunnite structure (orthorhombic II) for samples treated at pressure near 16 GPa around 1000 °C. Some *in situ* high-pressure x-ray-diffraction studies appear to support this phase change.[5,12] P-T boundaries have been calculated and compared with experiments[21,22] for the monoclinic-ortho I-ortho II (cotunnite) and the high-temperature tetragonal phase.

Despite all the confusion, the recent *in situ* high-pressure Raman and x-ray-diffraction study[15] on pure ZrO_2 has brought some finiteness to the subject and has shown, that when single-crystal ZrO_2 is pressurized at room temperature the following transformations occur consistently. With increasing pressure (1) monoclinic (baddeleyite) to orthorhombic I near 3.5 GPa, (2) ortho-

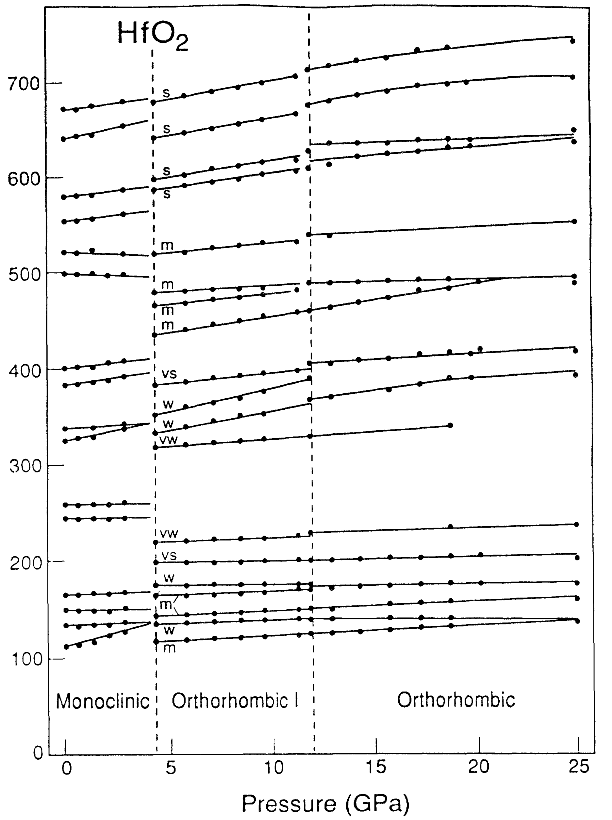

FIG. 6. Pressure dependence of the Raman peaks of HfO_2 to 25 GPa to show the $d\omega/dP$ behavior in more detail. The letters vw, w, m, s, and vs indicate the intensity of the Raman peaks. The dashed lines mark the transition pressure.

rhombic I to another unidentified structure (probably also another orthorhombic phase) near 13 GPa, and (3) then another transition at about 35 GPa, for which a tetragonal lattice different from that of the high-temperature tetragonal phase has been suggested. No positive evidence for the so-called cotunnite phase has been seen in the room-temperature *in situ* high-pressure experiment.[15]

A. The 4.3 GPa transition in hafnia

In view of the strong similarities that should exist between ZrO_2 and HfO_2, we may expect pressure-induced transition sequences of the same type for HfO_2. In fact, the recent Raman investigation by Arashi[17] on HfO_2 to 10 GPa has revealed such a similarity for the first pressure-induced phase transition that occurs in HfO_2 near 4.3 GPa. Arashi has found that the Raman spectral features of the high-pressure phase following this transition is very similar to that of the orthorhombic I phase of ZrO_2, and therefore has concluded that this high-pressure phase of HfO_2 is orthorhombic with the space-group symmetry *Pbcm*, as in the case of ZrO_2. This conclusion is well supported by the recent high-pressure *in situ* synchrotron x-ray-diffraction study of Adams, Leonard, and Russell[23] on HfO_2 and the x-ray study of Ohtaka, Yamanaka, and Kume,[24] on pressure-temperature treated hafnia. According to the former study, finely powdered HfO_2 begins to transform at 2.6 GPa when pressurized in the diamond cell, and the transformation is spread over a range of pressure. The resulting high-pressure phase has been successfully indexed on the basis of an orthorhombic unit cell with the space-group symmetry *Pbcm*, the same as the orthorhombic I phase of ZrO_2. The x-ray powder study on quenched HfO_2 (Ref. 22) from high-pressure–high-temperature fields of 4–5 GPa and 400–1000 °C has yielded results consistent with the orthorhombic I symmetry mentioned. Further, the possibility of another phase transition in HfO_2 at a higher pressure, > 10 GPa, has been suggested by Adams, Leonard, and Russell,[23] from the anomalous behavior of the *a* parameter of the orthorhombic I phase with pressure.

The results of our Raman study clearly show that three pressure-induced phase transitions occur in HfO_2 at 4.3 ± 0.2, 12 ± 0.5, and 28 ± 2 GPa. Of these the 4.3-GPa transition has already been identified as monoclinic to orthorhombic I, as discussed above.

B. The 12- and 28-GPa transition in hafnia

Our Raman data on HfO_2 are in excellent agreement with the Raman data of Arashi,[17] not only across the 4.3-GPa transition and also up to 10 GPa, the limit of

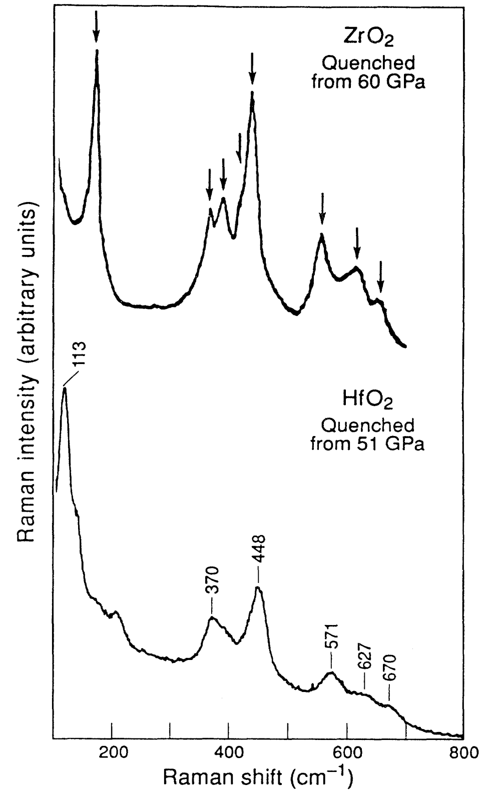

FIG. 7. A comparison of the Raman spectra of the quenched high-pressure phase of ZrO_2. The ZrO_2 data are from Arashi *et al.*[15] The strong resemblance suggests similar structure for the quenched high-pressure phase.

pressure reached in the latter investigation. The earlier study by Arashi *et al.*[15] on ZrO_2 strongly suggests two more high-pressure phase transitions for HfO_2 and the present study provides strong Raman evidence for these transitions. There are distinct changes in the Raman spectral features of HfO_2 near 12 and 30 GPa (see Figs. 3, 5, and 6). The changes at the 12 GPa transition are rather subtle, and in fact are very similar to those found by Arashi *et al.*[15] for ZrO_2 near 13 GPa. For this transition, another orthorhombic phase has been suggested. We believe that a similar transition occurs also in the case of HfO_2 near 12 GPa. This would also be consistent with the suggestion of Adams, Leonard, and Russell.[23] As for the transition in HfO_2 near 28 GPa, the Raman spectral features suggest a close similarity to the 35-GPa transition in ZrO_2. Although Arashi *et al.*[15] could not obtain *in situ* Raman data on ZrO_2 above 25 GPa, they were able to quench the high-pressure phase and record its Raman spectrum. A comparison of this spectrum with our *in situ* Raman spectra of the high-pressure phase as well as the quenched phase of HfO_2 reveals a strong similarity (see Fig. 7). This suggests that the two high-pressure phases might be structurally the same. For this high-pressure phase of ZrO_2 Arashi *et al.*[15] have suggested a tetragonal lattice. Pushing the analogy further we suggest the same structure for this pressure-induced phase of HfO_2.

Liu[14] has been able to quench a high-pressure phase of HfO_2 with cotunnite structure, from P-T fields of >16 GPa and 1000 °C. This phase appears to need high temperature. In this connection, it would be of great help to record the Raman spectrum of this phase for a comparison with the *in situ* high-pressure Raman spectra of hafnia.

C. Reversibility of the transitions

The monoclinic to the orthorhombic I transition in HfO_2 is found to be perfectly reversible with single-crystal samples. However, Ohtaka, Yamanaka, and Kume[24] were able to quench the orthorhombic I phase of HfO_2 down to ambient pressure. There are two factors which could contribute to the difference in behavior. First, the starting material in the latter study was finely powdered hafnia which had 2% ZrO_2 as impurity. Second, the orthorhombic I phase was formed under P-T conditions ranging from 4 to 6 GPa and 400 to 1000 °C. Of these factors, we believe that the grain size could be the principal one influencing the difference in behavior. Similar pattern in behavior with regard to reversibility has been noted in the case of ZrO_2.

Our finding of ready reversibility in HfO_2 to the starting monoclinic phase when pressure was released after reaching 25 GPa is significant. If the second high-pressure phase, stable between 12 and 28 GPa, had the cotunnite structure, we should have been able to quench this phase, as Liu[14] has shown. This then rules out cotunnite structure for the high-pressure phase that we find between 12 and 28 GPa.

The nonreversibility after the transition in HfO_2 near 28 GPa is consistent with the behavior of the pressure-induced phase transition in ZrO_2 near 35 GPa. The latter high-pressure phase of ZrO_2 was retained on release of pressure. The parallel behavior we believe supports the idea of similar structural sequence of HfO_2.

IV. FURTHER COMMENTS

In Table II the molar volume of the different phases of interest are given for ZrO_2 as well as HfO_2. The molar volumes of the corresponding phases for the two dioxides are nearly the same. This is to be expected since the size of the Hf and Zr ions are almost identical due to the effect of lanthanide contraction in the case of Hf. It is significant that the pressure-induced sequence of phase transitions occur in both materials at nearly the same pressure. Further, the $d\omega/dP$ of the Raman frequencies have similar slopes in the two materials. For these reasons we believe that the bulk modulus K_0 of HfO_2 cannot be very different from that of ZrO_2. We have therefore approximated K_0 of HfO_2 to 185 ± 20 GPa for the monoclinic (baddeleyite) phase, taking into account the value of 182 ± 20 GPa for ZrO_2 (Refs. 25 and 26) and the slightly smaller atomic volume of HfO_2 and applying the scaling law of Anderson and Nafe[27] between bulk modulus and specific volume. Adams, Leonard, and Russell[23] have given a value of $1.2 \times 10^{-3}\ \mathrm{GPa}^{-1}$ for the bulk compressibility of monoclinic HfO_2 which would result in $K_0 \sim 800$ GPa. This high value is difficult to reconcile with when one considers the pressure response of ZrO_2 and HfO_2; namely, the pressure dependence of the vibrational frequencies and pressure-induced phase

TABLE II. Molar volumes of the monoclinic (baddeleyite) and high pressure phases of ZrO_2 and HfO_2 in $\mathrm{cm}^3/\mathrm{mol}$.

	Monoclinic (baddeleyite)	Ortho I	Ortho II	Tetragonal
ZrO_2	21.113^{a}	20.22^{b}	18.13^{c} 17.64 (20 GPa)^{e}	17.12^{d} 15.4 (55 GPa)^{d}
HfO_2	20.82^{f}	20.04 (2.6 GPa)^{f}	17.86^{c}	
ZrO_2: $K_0 \sim 182 \pm 20^{g}$ GPa; HfO_2: K_0 (estimated) $\sim 185 \pm 20$ GPa^{h}				

[a] From x-ray density.
[b] Reference 7.
[c] Reference 14.
[d] Reference 15.
[e] Reference 12.
[f] Reference 23.
[g] References 25 and 26.
[h] See text for explanation of K_0 for HfO_2.

transitions.

A clearer and better understanding of the pressure-induced phase transitions in HfO_2 could result, by performing *in situ* Raman and x-ray-diffraction studies on single-crystal samples and on quenched samples. In particular, samples of HfO_2 could be laser heated in the diamond cell at several high-pressure points and then studied by Raman and x-ray studies *in situ*. Although such studies have been carried out on ZrO_2 in a limited sense, there has been no concerted effort in bringing Raman and x-ray-diffraction studies together to bear upon the problem of high-pressure–high-temperature phase stability in these systems. In this connection, the work of Arashi *et al.*[15] on ZrO_2 is the first of its kind and this study has led to a better picture. Both zirconia and hafnia are very important ceramic materials and a better understanding of their P-T behavior is bound to enhance their potential applications.

V. SUMMARY AND CONCLUSIONS

(1) Three pressure-induced phase transitions were observed in HfO_2 at 4.3, 12, and 28 GPa when single-crystal samples were pressurized with 4:1 methanol as pressure medium and at room temperature.

(2) The 4.3-GPa transition in HfO_2 has been identified as monoclinic ($P2_1/c$) to orthorhombic ($Pbcm$), from the Raman and high-pressure *in situ* x-ray-diffraction studies.

(3) The 12- and 28-GPa transitions in HfO_2 appear to be very similar to that of ZrO_2 and therefore similar structures are proposed for the high-pressure phases of HfO_2.

(4) From the close correspondence of the pressure-induced phase transitions in HfO_2 and ZrO_2 and from the almost identical response of the Raman modes to pressure for both materials, we conclude that the bulk modulii of HfO_2 and ZrO_2 should be very nearly the same.

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