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New high-pressure phase of ZrO_2 above 35 GPa

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Phase transformations of pure ZrO_2 at high pressure up to 60 GPa were investigated by using x-ray diffraction and micro-Raman-scattering methods. The existence of phase transformation at about 13 GPa was reconfirmed by the spectral change of *in situ* Raman scattering. A new phase transformation at 35 GPa was observed from both of the experimental methods employed. A new high-pressure phase is stable up to 60 GPa and quenchable to ambient conditions. The measured x-ray diffraction pattern for this high-pressure phase was indexed on the basis of tetragonal symmetry. Eight Raman bands were observed for the quenched high-pressure phase. Candidate space groups that are consistent with the obtained experimental results were deduced. The most plausible space group is considered as one of C_{4h}^1 , C_{4h}^4 , D_{4h}^1 , or D_{4h}^5 ($P4/m$, $P4_2/n$, $P4/mmm$, or $P4/mbm$). The molar volume for the new high-pressure phase is smallest in the high-pressure phases so far reported for ZrO_2 .

I. INTRODUCTION

Recently, phase transformation of ZrO_2 under high pressure has aroused much interest in material and geophysical researches. Zirconia ceramics have been investigated with emphasis on their toughness. The toughening mechanism of zirconia ceramics is explained by a transformation induced by a stress field.^{1,2} Thus the investigation of the phase transformation at high pressure in ZrO_2 , from a microscopic view point, is considered to be important. The investigations of pressure-induced phase transformation of ZrO_2 is also important in geophysical implications as the polymorphic structures of ZrO_2 might be possible in the high-pressure model for the polymorphs of SiO_2 .^{3,4} The pressure-induced phase transition of fluorite-type of CeO_2 has been observed at 30 GPa, and the crystal structure of high-pressure phase was compared with that of ZrO_2 .^{5,6}

The polymorphism of ZrO_2 at high pressures has been extensively studied.⁷⁻¹⁷ The stable phase of ZrO_2 at room-temperature and atmospheric pressure belongs to the monoclinic system. Two different crystal structures were reported for the high-pressure phase observed in the pressure range between 3.5 and 13 GPa at room temperature.

An orthorhombic crystal structure was deduced from x-ray diffraction and Raman spectroscopic studies.¹⁸ Kudoh *et al.* have made an *in situ* structural analysis of a

single crystal ZrO_2 using a diamond-anvil pressure cell and concluded that the space group of the high-pressure phase was orthorhombic $Pbcm$ (D_{2h}^{11}).¹⁹ This result has recently been confirmed by Heuer *et al.*²⁰ from a transmission electron microscopic observation of a ZrO_2 thin film.

A tetragonal structure that was different from the high-temperature tetragonal phase was also reported for the high-pressure phase observed above 3.5 GPa.^{21,22}

At pressures higher than 13 GPa, a different orthorhombic phase with the cotunnite-type structure was reported by Block *et al.*²¹ and Liu.³ Recently, Ohtaka *et al.*^{23,24} have reported that the orthorhombic phase observed above 3.5 GPa (which they newly denoted as ortho I) transformed to the orthorhombic phase (ortho II) at 16 GPa and 600 °C from the quenching experiments of fine powder of ZrO_2 containing 2 mol % Y_2O_3 . They have determined the phase boundary between the ortho I and ortho II phase and concluded that ortho II had the cotunnite-type crystal structure.

More extensive investigations at higher pressure are necessary to resolve these controversies regarding the crystal structure of high-pressure phases and to clarify the nature of the successive pressure-induced phase transformations of ZrO_2 . The purpose of this study is to clarify the phase transformation behavior of ZrO_2 at the higher-pressure region above 20 GPa using x-ray diffraction and micro-Raman-spectroscopic techniques.

II. EXPERIMENT

Single crystals of ZrO_2 were grown from PbF_2 flux using a platinum crucible in the region of temperature where the monoclinic phase is stable.

Pressure was generated using a lever-type diamond-anvil cell²⁵ and measured by using the ruby fluorescence method.²⁶ Diamond anvils with a 0.5-mm culet were used. Stainless steel 0.2 mm in thickness was used for gasketing. After preindention to 40 μm in thickness, the gasket had a hole 100 μm in diameter at the center of the indented region. The powdered ZrO_2 obtained from grinding the synthesized single crystal were contained into the hole of the gasket. For *in situ* x-ray measurements at high pressures, the powdered ZrO_2 sample that passed through a 600 mesh sieve was used. For *in situ* Raman measurements and quenching experiments, larger crystals (40 μm in diameter) were used. Distilled water was employed as pressure transmitting media.

X-ray diffraction measurements were made by using a high-power rotating-anode x-ray source (Rigaku RU-200). $Mo K_\alpha$ radiation filtered by a Zr foil 50- μm thick was collimated using a collimator with 80 μm pinholes. X-ray diffraction pattern was recopted on a nonscreen type x-ray film. The d spacings were determined by measuring the diameter of diffraction rings and the camera constant.

Raman spectra were obtained using a micro-Raman system, which consists of a double monochromator (JASCO CT-1000D) combined with an optical microscope. An objective lens with 40 or 10 magnification was used. For excitation both 514.5- and 488.0-nm oscillation lines of Ar-ion laser (NEC GLG 3200) were used at a power level of 300 mW. Spectra were recorded with a conventional photon counting system.

III. RESULTS AND DISCUSSION

The observed pressure dependence of d spacings of ZrO_2 is presented in Fig. 1. Phase transformation can be

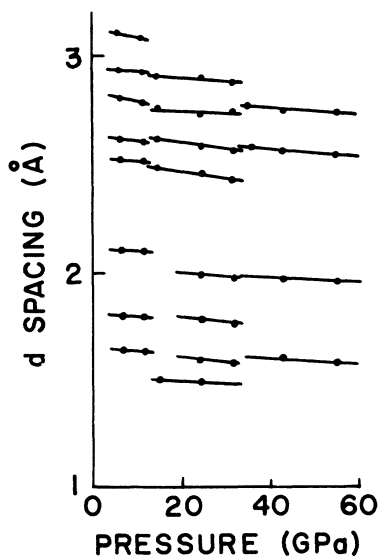


FIG. 1. Pressure dependence of d spacings of ZrO_2 .

recognized from the discontinuity of d spacings at about 13 GPa. The diffraction pattern measured at 25 GPa is shown in Fig. 2(a). The transition pressure is the same as that reported by Ohtaka *et al.* However, the diffraction pattern shown in Fig. 2(a) does not agree with that of Ohtaka *et al.*²³ The phase transformation at 13 GPa was reconfirmed, but from our experimental results, it is difficult to conclude that the high-pressure phase that appeared above 13 GPa has the cotunnite-type crystal structure.

Another phase transformation was observed at about 32 GPa. This high-pressure phase is stable up to 60 GPa, which is the maximum pressure attained in the present experiment. The diffraction pattern measured at 55 GPa is presented in Fig. 2(b) and the obtained d spacings are shown in the upper part of Table I. The analysis of crystal structure for this high-pressure phase is in progress, and observed diffraction peaks are indexed on the basis of tetragonal symmetry as shown in Table I.²⁷ It is also found that this high-pressure phase is quenchable to atmospheric pressure when the diamond-anvil pressure cell is unloaded to atmospheric pressure within 10 min. The diffraction pattern of the quenched sample is presented in Fig. 2(c) and the d spacings are also given in Table I(b). The diffraction pattern is similar to that of measured at 55 GPa. For the quenched sample, micro-Raman spectra were measured.

Peak shifts of Raman spectra measured at various pressures are presented in Fig. 3. The spectral change at 3.5 GPa, which was already reported, is not shown in Fig. 3. Phase transformation is confirmed from the spectral change at about 13 GPa. Sixteen Raman bands are ob-

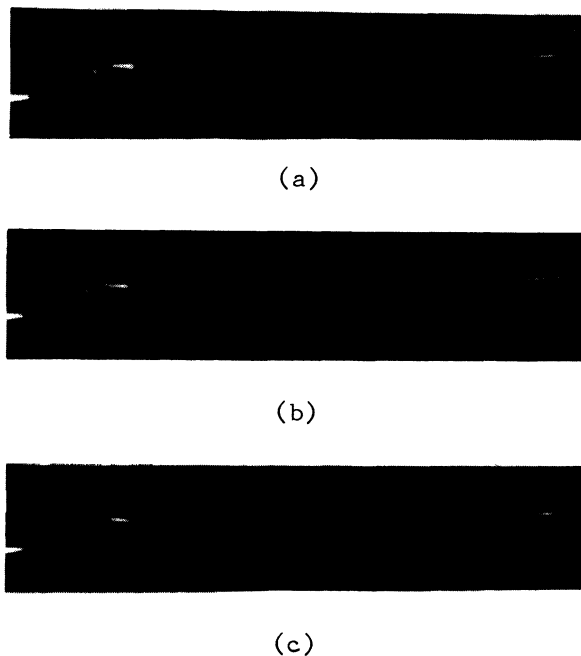


FIG. 2. Observed x-ray diffraction pattern of the high-pressure phase of ZrO_2 . (a) Measured at 25 GPa (ortho phase). (b) Measured at 55 GPa (new tetragonal phase). (c) Quenched sample from 60 GPa. The diffraction pattern is similar to (b).

TABLE I. Observed and calculated d spacings for ZrO₂ in tetragonal high-pressure phase ($Z=4$). The upper part was observed at 55 GPa; $a=4.52$ Å, $c=5.01$ Å. The lower part was the quenched phase from 60 GPa; $a=4.66$ Å, $c=5.24$ Å.

$h k l$	$d_{(\text{obs.})}(\text{Å})$	$d_{(\text{calc.})}(\text{Å})$
(111)	2.72	2.69
(002)	2.53	2.51
(112)	1.95	1.97
(220)	1.58	1.59

$h k l$	$d_{(\text{obs.})}(\text{Å})$	$d_{(\text{calc.})}(\text{Å})$
(111)	2.81	2.79
(002)	2.63	2.61
(112)	2.04	2.05
(220)	1.63	1.64

served for the higher-pressure phase at 15 GPa. The transformation pressure agreed with that reported by Oh-taka *et al.*²⁴ From the Raman spectroscopic studies, there is no experimental evidence to conclude that the higher-pressure phase observed above 13 GPa has the cotunnite-type crystal structure. It is reasonable that this higher-pressure phase belongs to the crystal system having the lower symmetry such as orthorhombic from the large number of observed Raman bands. Further experiments combined with x-ray diffraction are necessary to clarify the crystal structure of the high-pressure phase observed above 13 GPa.

In situ Raman spectroscopic studies at the higher

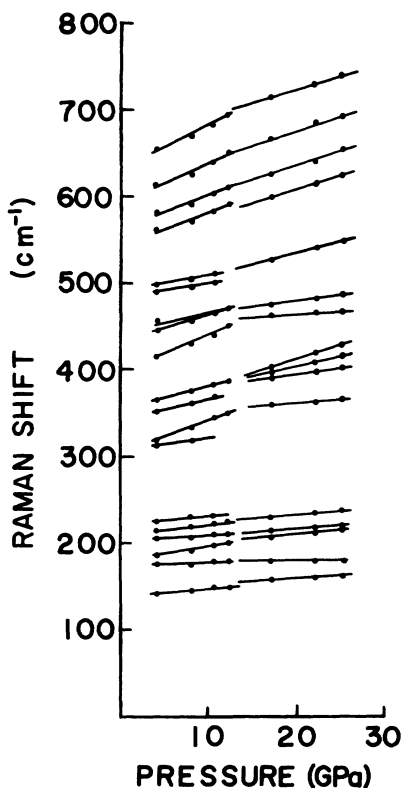


FIG. 3. Pressure dependence of Raman spectra of ZrO₂.

pressures above 40 GPa were intended to clarify the high-pressure phase, which is found above 35 GPa through the present *in situ* x-ray diffraction experiments. As micro-Raman system for the specimen contained in the diamond-anvil pressure cell requires an objective lens with long working distance, the numerical aperture of objective lens is limited to a small value, which makes the measurement of weak Raman spectra difficult. Generally, Raman intensity becomes weak with increasing pressure, and therefore a reliable *in situ* Raman spectra was not obtained in the pressure regions above 30 GPa in these experiments.

Micro-Raman spectra of the small ZrO₂ crystal quenched from 60 GPa are measured at room temperature using an objective lens with large numerical aperture (0.65) at ambient condition. The observed spectra shown in Fig. 4 have eight Raman bands. This small number of Raman band indicates that the quenched phase has a crystal structure with high symmetry. This experimental fact agrees with the result obtained from the preliminary structural analysis of the quenched sample using x-ray diffraction techniques. Since distilled water is used as pressure transmitting media, it is necessary to check the possibility of the formation of hydrous ZrO₂ at high pressure. A Raman band near 3300 cm⁻¹ is useful for this check because the Raman band observed in this region corresponds to stretching modes of OH-bond contained in the crystal.²⁸ As no Raman were observed in this wave number region, the quenched ZrO₂ crystal remained in a nonhydrous state.

Using the results obtained from x-ray diffraction and Raman spectroscopic studies, the plausible crystal structure for the high-pressure phase newly found above 35 GPa was investigated. Zr atoms are arranged so as to make a distorted face centered lattice in monoclinic, orthorhombic, and tetragonal phases. Assuming that Zr atoms are also situated on distorted face centered lattice sites in the high-pressure phase, the possible space group are deduced from tetragonal symmetry. This assumption is consistent with the indexing of the observed strong x-ray diffraction peaks in which the Zr metal is mainly contributed. The indices of strong peaks satisfy the $h+k=2n$ condition that is required for the atoms situated at $\{(0,0,0), (\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2})\}$, $\{(0,0,z), (\frac{1}{2}, \frac{1}{2}, z)\}$

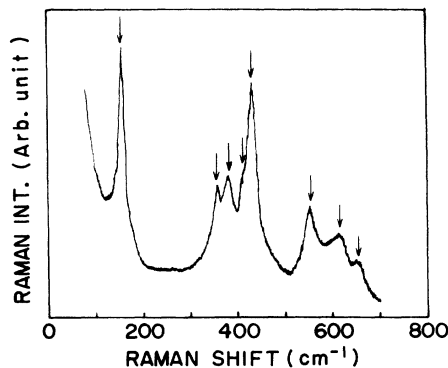


FIG. 4. Micro-Raman spectra of quenched ZrO₂ from 60 GPa.

or $\{(\frac{1}{2}, 0, z), (0, \frac{1}{2}, z)\}$ in tetragonal symmetry. The possible space groups are listed in Table II. The number of Raman bands and irreducible representations expected from factor-group analysis for deducing space groups are also presented in Table II. A large number of Raman bands are expected for the space group that has no inversion symmetry. As eight Raman bands are observed for the high-pressure phase as shown in Fig. 4, it is concluded that the crystal structure of a new high-pressure phase has an inversion symmetry and the most plausible space group is one of C_{4h}^1 , C_{4h}^2 , D_{4h}^1 , or D_{4h}^2 ($P4/m$, $P4_2/n$, $P4/mmm$, or $P4/mbm$).

Alzyab *et al.*²² have been reported that above 4 GPa at room temperature, pure ZrO_2 transformed to a "new" tetragonal phase, which was different from the one obtained at high temperatures at atmospheric pressure. They have observed 19 Raman bands for the tetragonal phase at high pressures. On the other hand, Raman scattering measurements for the tetragonal high-pressure, which was newly found from our investigations, showed eight Raman bands. From the difference in the number of observed Raman bands, it is concluded that the new tetragonal phase observed above 35 GPa is different from the one reported by Alzyab *et al.*

On the basis of the determined crystal structure, the pressure dependence of molar volume of a newly observed high-pressure phase is deduced as shown in Fig. 5. In this figure, the values obtained by Ming and Manghnani,¹¹ Liu,³ and Ohtaka *et al.*²⁴ are also shown. The newly observed tetragonal high-pressure phase has the highest density. The molar volume change for the phase transformation at 35 GPa between orthorhombic II and new tetragonal high-pressure phase is 3.8%. From the pressure dependence of molar volume, it is concluded that the compressibility for the tetragonal high-pressure phase is smaller than that of the orthorhombic I or orthorhombic II high-pressure phase.

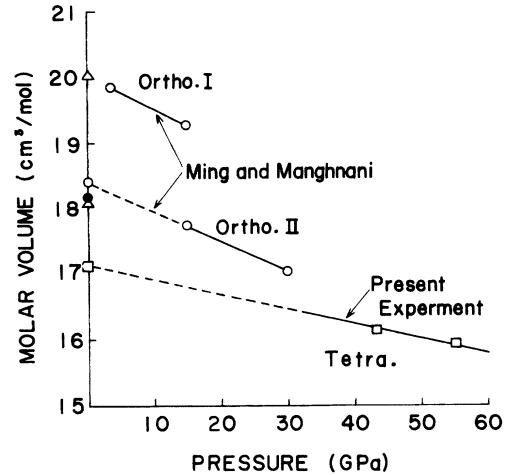


FIG. 5. Pressure dependence of molar volume of high-pressure phases of ZrO_2 . \circ , Ming and Manghnani; Δ , Ohtaka *et al.*; \bullet , Liu; \square , this experiment.

IV. CONCLUSIONS

The phase transformation of pure ZrO_2 at 13 GPa was reconfirmed from *in situ* micro-Raman scattering and x-ray diffraction experiments. From our experimental results, it is difficult to conclude that the crystal structure for high-pressure phase observed above 13 GPa is cotunnite type. From the number of observed Raman band, it can be considered that this high-pressure phase belongs to crystal system having the lower symmetry such as orthorhombic. Another phase transformation of ZrO_2 was found at 35 GPa. This new phase is stable up to 60 GPa and quenchable to atmospheric pressure. Micro-Raman measurements showed eight Raman bands for the quenched sample. The space group for the new high-pressure phase was selected so as to satisfy the x-ray ex-

TABLE II. The space groups which satisfy the extinction rules of x-ray diffraction observed for the new high-pressure phase of ZrO_2 . ($Z=4$). The number of Raman active irreducible representation is deduced from factor-group analysis.

Space group	Zr sites	O sites	Raman-active irreducible representations
$C_4^1 (P4)$	1a, 1b, 2c	4d, 4d	$8A + 7B + 9E$
$S_4^1 (P\bar{4})$	1a, 1c, 2g	4h, 4h	$7A + 8B + 9E$
$C_{4h}^1 (P4/m)$	1a, 1c, 2f	8l	$3A_g + 3B_g + 3E_g$
$C_{4h}^3 (P4/n)$	2a, 2c	8g	$4A_g + 4B_g + 5E_g$
$C_{4h}^4 (P4_2/n)$	4c	8g	$3A_g + 3B_g + 3E_g$
$D_4^1 (P422)$	1a, 1c, 2f	8p	$3A_1 + 3B_1 + 4B_2 + 9E$
$D_4^2 (P42_12)$	2a, 2c	8g	$4A_1 + 4B_1 + 3B_2 + 9E$
$C_{4v}^1 (P4mm)$	1a, 1b, 2c	4d, 4d	$6A_1 + 3B_1 + 4B_2 + 9E$
$C_{4v}^2 (P4bm)$	2a, 2b	8d	$4A_1 + 3B_1 + 4B_2 + 9E$
$D_{2d}^1 (P\bar{4}2m)$	1a, 1d, 2f	4n, 4n	$4A_1 + 2B_1 + 6B_1 + 9E$
$D_{2d}^3 (P\bar{4}2_1m)$	2a, 2c	8f	$4A_1 + 4B_1 + 4B_2 + 9E$
$D_{2d}^5 (P4m2)$	1a, 1b, 2g	8l	$4A_1 + 3B_1 + 6B_2 + 9E$
$D_{2d}^7 (P\bar{4}b2)$	2a, 2d	8i	$3A_1 + 4B_1 + 5B_2 + 9E$
$D_{4h}^1 (P4/mmm)$	1a, 1c, 2e	8r	$2A_{1g} + B_{1g} + 2B_{2g} + 3E_g$
$D_{4h}^3 (P4/nbm)$	2a, 2d	8m	$2A_{1g} + B_{1g} + 3B_{2g} + 5E_g$
$D_{4h}^5 (P4/mbm)$	2a, 2c	8k	$2A_{1g} + B_{1g} + 2B_{2g} + 3E_g$
$D_{4h}^7 (P4/nmm)$	2a, 2c	8j	$3A_{1g} + 2B_{1g} + 2B_{2g} + 5E_g$

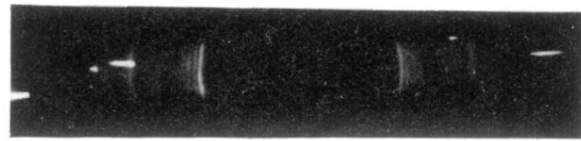
inction rules and to agree that the observed number of Raman band with the number expected from factor-group analysis. The most plausible space group is one of C_{4h}^1 , C_{4h}^4 , D_{4h}^1 , or D_{4h}^4 . Zr atoms locate at the distorted face-centered lattice site and are surrounded by eight oxygen atoms in the deduced crystal structure. The density

of the newly observed tetragonal high-pressure phase is about 3.8% higher than that of orthorhombic II phase.

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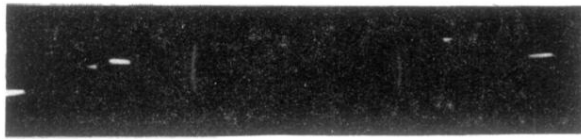
- ¹T. K. Gupta, F. F. Lange, and J. H. Bechtold, *J. Mater. Sci.* **13**, 1464 (1978).
- ²W. M. Kriven, *J. Am. Ceram. Soc.* **71**, 1021 (1988).
- ³L. Liu, *J. Phys. Chem. Solids* **41**, 331 (1980).
- ⁴L. Liu and W. A. Basset, in *Elements, Oxides, and Silicates: High-Pressure Phases with Implications for the Earth's Interior* (Oxford University Press, New York, 1986), p. 250.
- ⁵G. A. Kourouklis, A. Jayaraman, and G. P. Espinosa, *Phys. Rev. B* **37**, 4250 (1988).
- ⁶S. J. Duclos, Y. K. Vohra, and A. L. Ruoff, *Phys. Rev. B* **38**, 7755 (1988).
- ⁷E. D. Whitney, *J. Electrochem. Soc.* **112**, 91 (1965).
- ⁸G. L. Kulcinski, *J. Am. Ceram. Soc.* **51**, 582 (1968).
- ⁹G. Boquillon and C. Susse, *Rev. Internat. Hautes Temp. Refract.* **6**, 263 (1969).
- ¹⁰L. M. Lityagina, S. S. Kabalinka, T. A. Pashkina, and A. I. Khozyainov, *Fiz. Tverd. Tela (Leningrad)* **20**, 3475 (1978) [*Sov. Phys.—Solid State* **20**, 2009 (1978)].
- ¹¹L. C. Ming and M. H. Manghnani, in *Solid State Physics under Pressure: Recent Advances with Anvil Devices*, edited by S. Minomura (KTK Science, Tokyo, 1985), p. 135.
- ¹²R. Suyama, H. Takubo, and S. Kume, *J. Am. Ceram. Soc.* **68**, C-237 (1985).
- ¹³R. Suyama, T. Ashida, and S. Kume, *J. Am. Ceram. Soc.* **68**, C-134 (1985).
- ¹⁴H. Arashi, T. Suzuki, and S. Akimoto, *J. Mater. Sci. Lett.* **6**, 106 (1987).
- ¹⁵H. Arashi, in *High-Pressure Research in Mineral Physics: The Akimoto Volume*, edited by M. H. Manghnani and Y. Syono (Terra Sci. Am. Geophys. Union, Tokyo, Washington, D.C., 1987), p. 335.
- ¹⁶H. Arashi, O. Shimomura, T. Yagi, S. Akimoto, and Y. Kudoh, *Adv. Ceram.* **24**, 493 (1988).
- ¹⁷S. B. Qadri, E. F. Skelton, C. Quinn, and C. Gilmore, *Phys. Rev. B* **38**, 13 415 (1988).
- ¹⁸H. Arashi and M. Ishigame, *Phys. Status Solidi A* **71**, 313 (1982).
- ¹⁹Y. Kudoh, H. Takeda, and H. Arashi, *Phys. Chem. Miner.* **13**, 233 (1986).
- ²⁰A. H. Heuer, V. Lanteri, S. C. Farmer, R. Chaim, R. R. Lee, B. W. Kibbel, and R. M. Dickerson, *J. Mater. Sci.* **24**, 124 (1989).
- ²¹S. Block, J. A. H. da Jornada, and G. J. Piermarini, *J. Am. Ceram. Soc.* **68**, 497 (1985).
- ²²B. Alzyab, C. H. Perry, and R. P. Ingel, *J. Am. Ceram. Soc.* **70**, 760 (1987).
- ²³O. Ohtaka, T. Iwami, K. Urabe, and S. Kume, *J. Am. Ceram. Soc.* **71**, C-164 (1988).
- ²⁴O. Ohtaka, S. Kume, and E. Ito, *J. Am. Ceram. Soc.* **71**, C-448 (1988).
- ²⁵H. Arashi, A. Kaimai, S. Sasaki, W. Funato, and T. Sugawara, *Bull. Res. Inst. Sci. Measure. Tohoku Univ.* **32**, 27 (1984).
- ²⁶J. D. Barnett, S. Block, and G. J. Piermarini, *Rev. Sci. Instrum.* **44**, 1 (1973).
- ²⁷Y. Kudoh, C. T. Prewitt, and H. Arashi, *EOS Trans. Am. Geophys. Union*, **70**, 491 (1989).
- ²⁸A. Novak, in *Structure and Bonding 18*, edited by J. D. Dunitz (Springer-Verlag, Berlin, 1974), p. 177.



(a)



(b)



(c)

FIG. 2. Observed x-ray diffraction pattern of the high-pressure phase of ZrO_2 . (a) Measured at 25 GPa (ortho phase). (b) Measured at 55 GPa (new tetragonal phase). (c) Quenched sample from 60 GPa. The diffraction pattern is similar to (b).