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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Phase diagram and equation of state of ZrO_2 and HfO_2 at very high P and T	**Experiment number**: HS-1886
Beamline: ID30	**Date of experiment**: from: 06-OCT-02 to: 10-OCT-02	**Date of report**: 01/09/03
Shifts: 15 shifts	**Local contact(s)**: Dr. Mohamed MEZOUAR	*Received at ESRF:*

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Report:

ZrO_2 and HfO_2 are well-known major ceramic materials. They show the same sequence of high-pressure transitions. Monoclinic baddeleyite-type structure sequentially transforms to two orthorhombic phases under pressures; a distorted fluorite-type structure and then a cotunnite($PbCl_2$)-type structure. Recently, both experimental and theoretical studies show that cotunnite-type of ZrO_2 and HfO_2 have remarkably large values of bulk modulus ranging from 300 to 450 GPa. The considerable variation of reported bulk modulus indicates there are large experimental uncertainties to obtain compression curves. Since cotunnite-type of both ZrO_2 and HfO_2 are quenchable to ambient conditions, these are candidates for super-hard materials. The correct data of their elastic properties are, therefore, of great importance. In the present study, we have collected X-ray diffraction data up to 100 GPa in order to obtain reliable EOS of cotunnite-type ZrO_2 using sample annealing technique with IR-laser. We have also determined the phase relations of ZrO_2 using in situ laser heating technique. (We could not conduct the experiments for HfO_2 because of the limited beam time.)

The starting material was a fine powder of pure ZrO_2 (99.9 %) provided by Tosoh Co. Japan. The powder was mixed with about 1 wt % of platinum black, which works as an absorber of the YAG laser for heating and also provides an optimum pressure measurement. We used membrane type DAC. Two types of pressure transmitting medium were used; KCl for very high pressures (100 GPa) with annealing and Ar for in situ high temperature (4000 K) experiments at medium pressures (30 GPa),

respectively. To obtain reliable compression data free from deviatoric stresses, samples were first annealed at moderate temperatures (1000-1200 K) at each pressure condition, and then the diffraction data were recorded at room temperature (Andrault et al. 2000, Fiquet et al. 2000, Kuntz et al. 1996). Monochromatic X-ray beam was used in association with image plates to collect data over a 2theta interval from 4 to 25° using an on-line reader and FIT2D program. Obtained data were analyxed using GSAS program.

Figure 1 shows the obtained compression curve of cotunnite-type ZrO_2 to 100 GPa. Post-cotunnite phase was not observed up to this pressure range. This compression curve gives a set of bulk moduli (k_0) and its pressure derivative (k_0') of 278 GPa and 3.7 while k_0 is 267 GPa with fixed K_0' at 4. These bulk modulus are close to our previous study (Ohtaka et al. 2001), where sample annealing technique was also used, but much smaller than those obtained by room temperature compression using DAC without annealing nor pressure transmitting medium (Desgrenier et al. 1999 and Haines et al. 1995). Accordingly, in DAC experiments at room temperature, special attention should be paid to deviatoric stress which makes apparent pressures high and consequently gives a large values of bulk modulus.

Figure 2 summalizes the results of in situ high T-P observations. Although the exact T-P conditions were difficult to determine, it should be noted that cubic phase that is supposed to exist at high temperature regime was not observed in the present study. Instead, tetragonal and cotunnite (orthoII) phases were confirmed to be stable up to 3000 K. Detailed high temperature in situ experiments at moderate pressure range is needed.

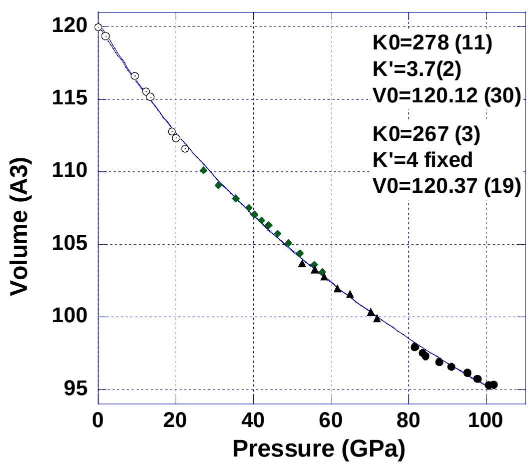

Fig. 1 EoS of cotunnite-type ZrO_2

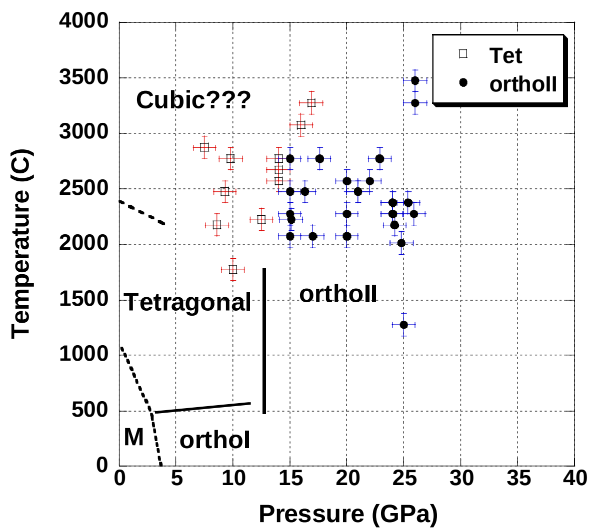

Fig. 2 Phase relations at high temperatures

References
Andrault, D et al. (2000), *Am. Mineral.*, 85, 364-71.
Desgreniers, S and K. Lagarec (1999), *Phys. Rev. B,* 59, 8467-72.
Fiquet, G et al. (2000), *Geophysical Research Lett.*, 27, 21-24.
Haines, J et al. (1995), J. Am. Ceram. Soc. 78, 445-449.
Kunz M.et al. (1996), *Am. Mineral.*, 81, 1528-31, 1996.
Ohtaka, O et al. (2001), *Phys. Rev. B* 63, 174108-1-8.