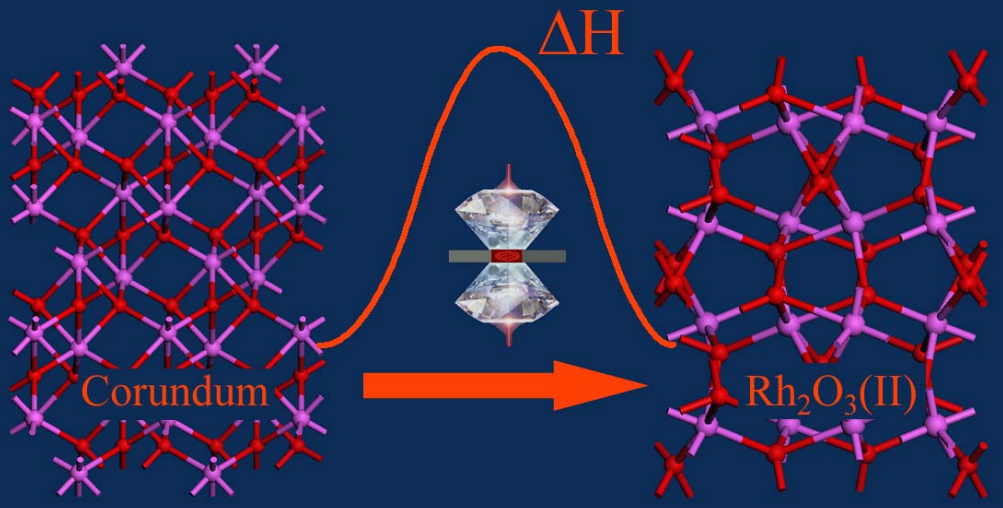

Study of transformation mechanism for the corundum-to-Rh_2O_3(II) transition in Al_2O_3

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Advisor: Jianjun Dong[1]
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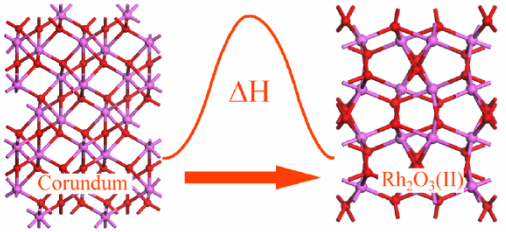
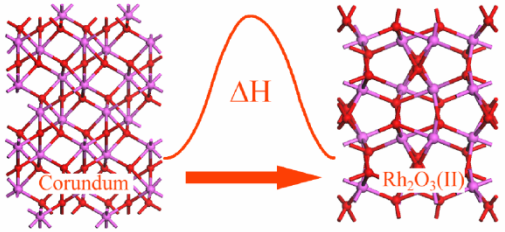
2009 COMPRES Annual Meeting

Outline



- Background
  - Experiments
  - Equilibrium T-P Phase Diagram
- Transformation Mechanism
  - Transition Path
  - Kinetic Barriers and Pressure Effect
  - Metastability
- Properties: Corundum vs. Rh_2O_3(II)
  - Elastic Properties
  - Raman Frequencies

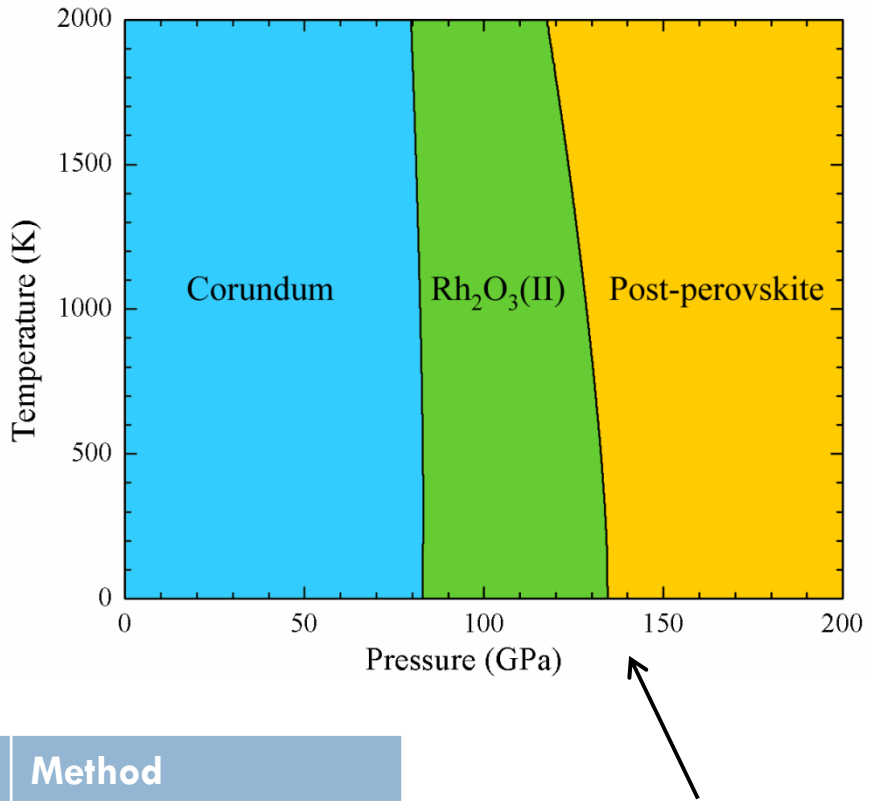
High-Pressure Phase Transition



- Corundum phase:
  stable up to 175 GPa, *without heating*
  [A. P. Jephcoat *et al.* 1988].

- Corundum-to-Rh_2O_3(II) transition:
  observed at 79–100 GPa & *>1000 K*
  [See table below].

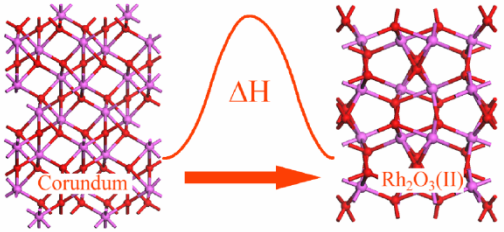
- Rh_2O_3(II) phase:
  observed >85 GPa on decompression
  [J. F. Lin *et al.* 2004].



Experiments	Corundum-to-Rh_2O_3(II)	Method
N. Funamori *et al.* (1997)	~100 GPa (~1000 K)	XRD (LH-DAC)
T. Mashimo *et al.* (2000)	79 GPa (1133 K)	Shock Compression
J. F. Lin *et al.* (2004)	96 GPa (1200 K)	XRD (LH-DAC)

LDA-DFT

Structural Similarity



Comparison of corundum and Rh_2O_3(II) structures

	Corundum	Rh_2O_3(II)
Crystal Class	Rhombohedral	Orthorhombic
Space Group	R-3c	Pbcn
Coordination: O	Al_4O	Al_4O
Coordination: Al	AlO_6	AlO_6
AlO_6 octahedron sharing	1 face, 3 edge, 9 corner	1 face, 2 edge, 11 corner

Corundum structure (rhombohedral) can be viewed as a monoclinic lattice, which is closely related to the orthorhombic Rh_2O_3(II) phase.

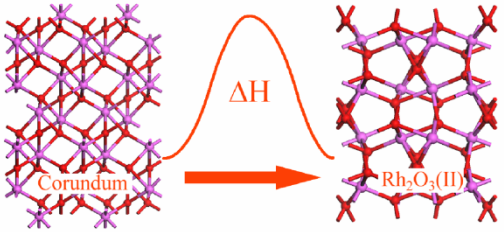
Corundum: Rhombohedral (R-3c) ⟶ Monoclinic (P2/c) †

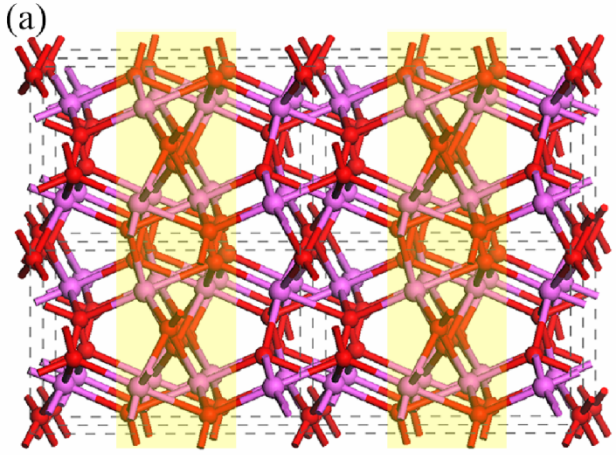
Corundum ⟷ (Monoclinic, P2/c) Rh_2O_3(II)

20 atom per unit cell†

† H. Stokes and D. Hatch

Structural Similarity



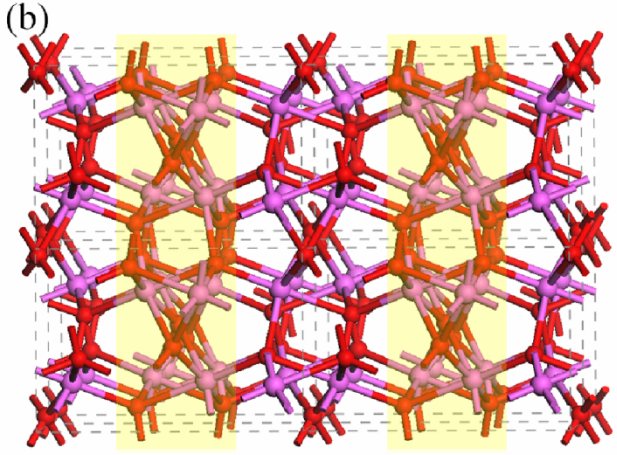


$$\begin{pmatrix} a_m \\ b_m \\ c_m \end{pmatrix} = \begin{pmatrix} 1 & 1 & -1 \\ 1 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} a_r \\ b_r \\ c_r \end{pmatrix}$$

$$\begin{pmatrix} a_m & 0 & 0 \\ 0 & b_m & 0 \\ c_m \cdot \cos\beta & 0 & c_m \cdot \sin\beta \end{pmatrix}$$

h: hexagonal
r: rhombohedral
m: monoclinic

$$\begin{pmatrix} a_r \\ b_r \\ c_r \end{pmatrix} = \begin{pmatrix} \frac{1}{2}a_h & \frac{\sqrt{3}}{6}a_h & \frac{1}{3}c_h \\ -\frac{1}{2}a_h & \frac{\sqrt{3}}{6}a_h & \frac{1}{3}c_h \\ 0 & -\frac{\sqrt{3}}{3}a_h & \frac{1}{3}c_h \end{pmatrix}$$

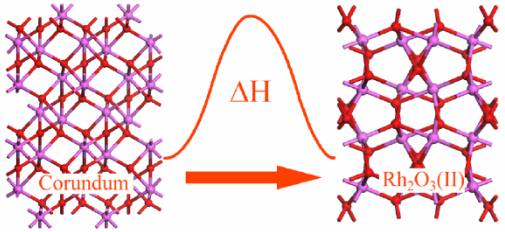


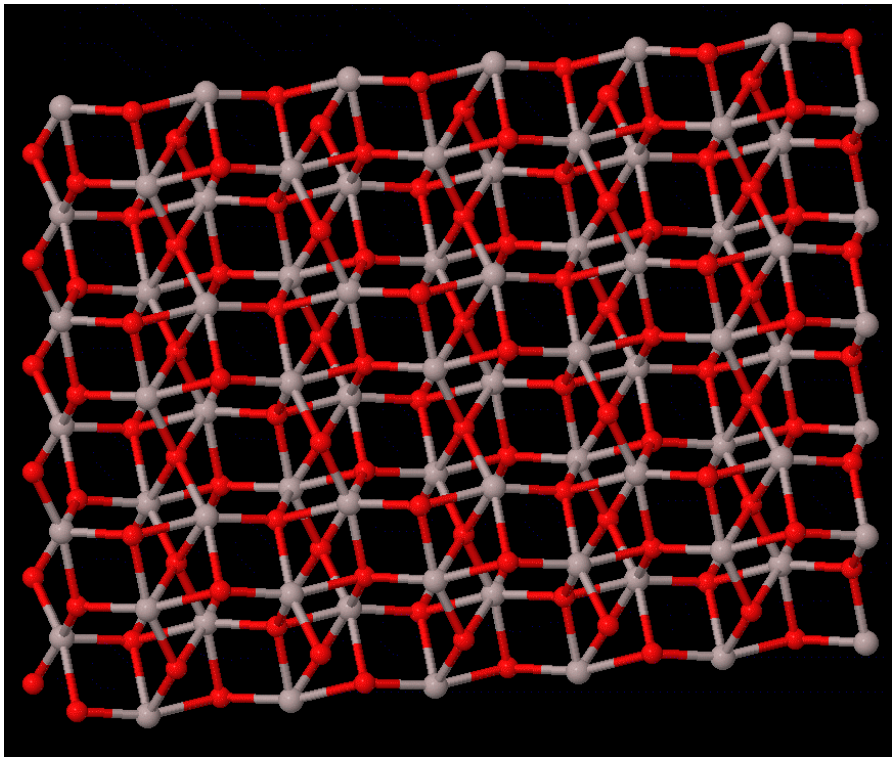
$$a_m = \sqrt{\frac{4}{3}a_h^2 + \frac{1}{9}c_h^2} \quad b_m = a_h \quad c_m = \sqrt{\frac{1}{3}a_h^2 + \frac{1}{9}c_h^2} \quad \beta = \cos^{-1}\left[(\frac{2}{3}a_h^2 - \frac{1}{9}c_h^2)/(a_m \cdot c_m)\right]$$

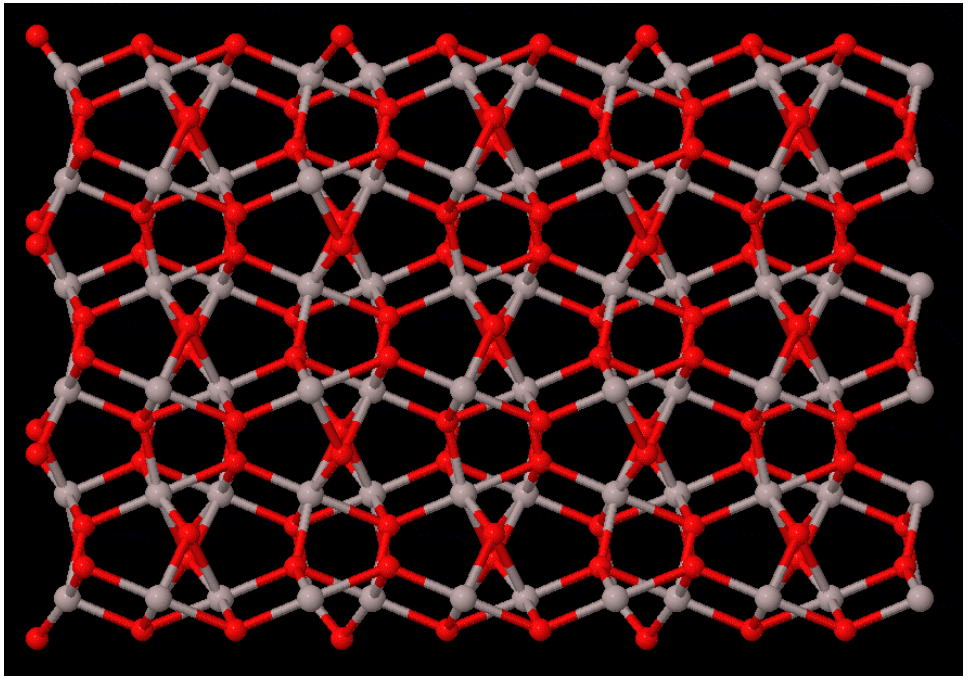
Structures of (a) Corundum and (b) $Rh_2O_3(II)$ Phases

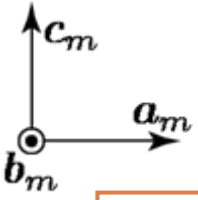
84 GPa	Corundum	$Rh_2O_3(II)$
a (Å)	6.481	6.472
b (Å)	4.426	4.438
c (Å)	4.732	4.600
β	95.26°	90°

Transformation Path

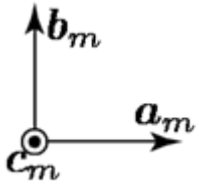








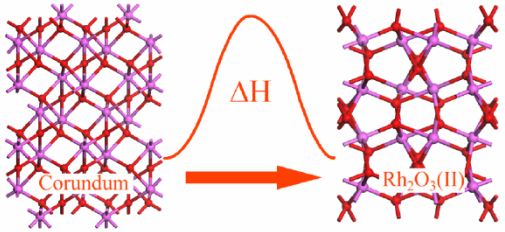
Viewed from b-axis

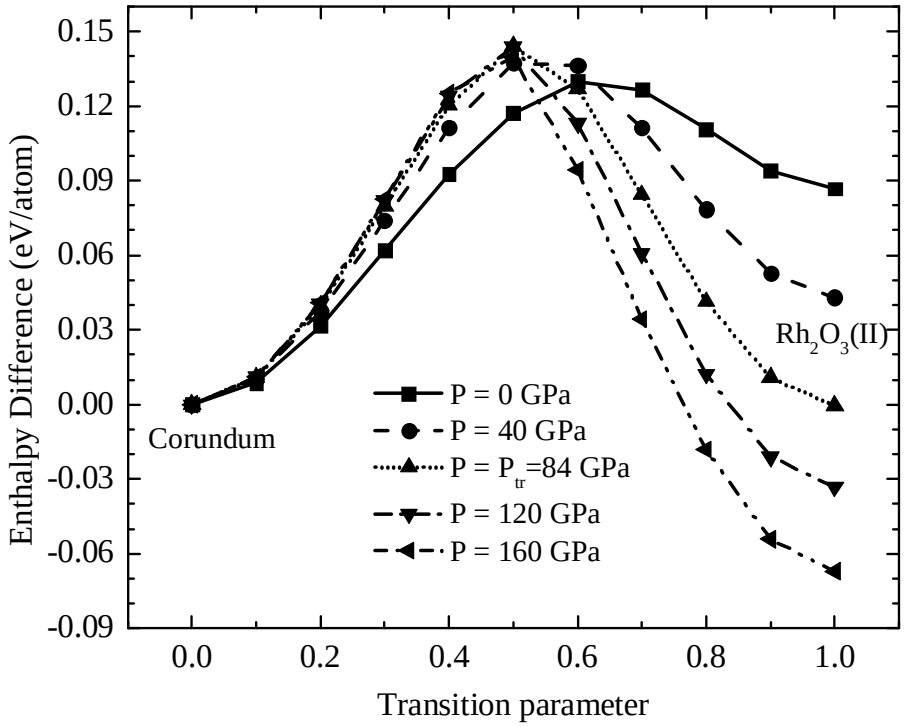


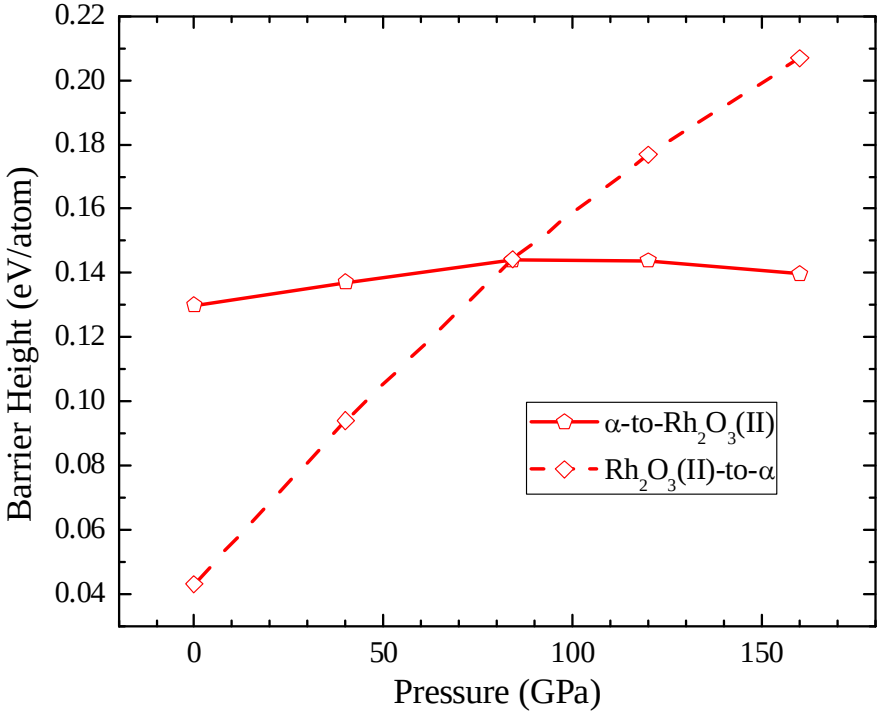
Viewed from c-axis

[1]4g-site O and [1]4g-site Al atom: One Bond Breaking-and-Reforming (OB-BAR)

Kinetic Barrier Heights





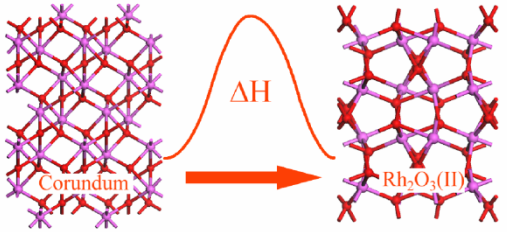


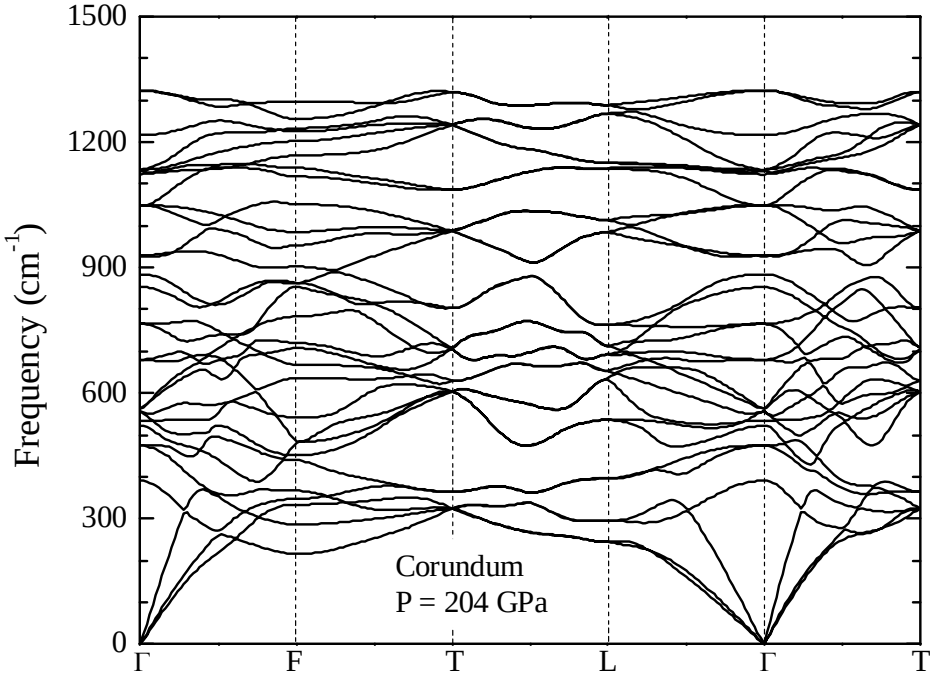
- The backward barrier height decrease significantly upon decompression.

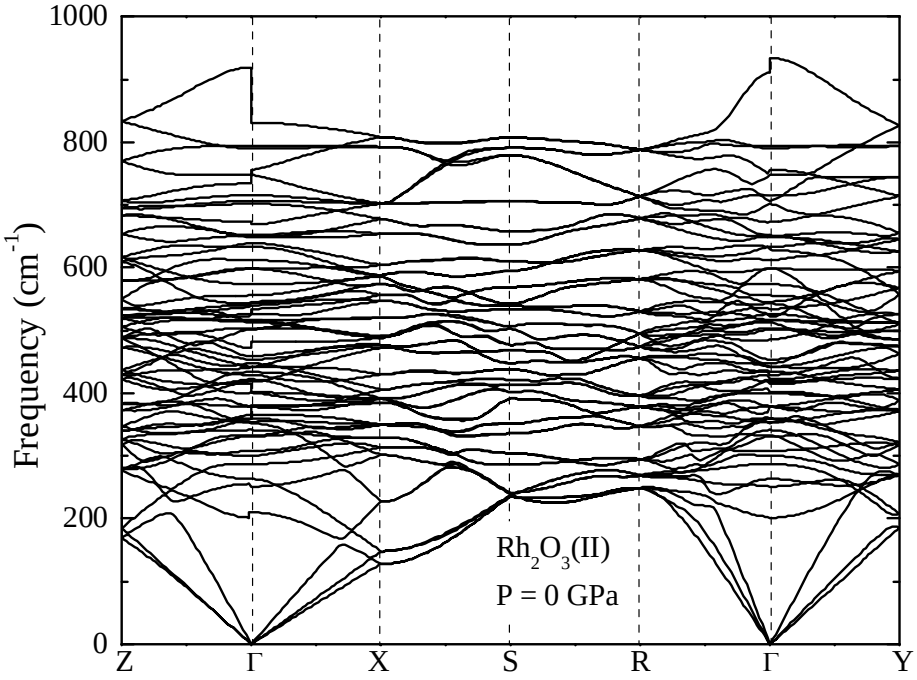
- The Rh_2O_3(II) phase is unlikely to be quenchable to low pressures.

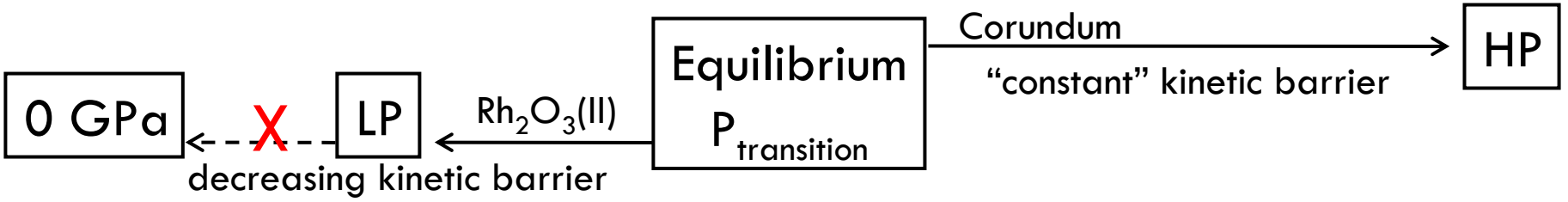
Barrier Height	0 GPa	84 GPa	160 GPa
Forward	130 meV	144 meV	140 meV
Backward	43 meV	144 meV	207 meV

Metastability

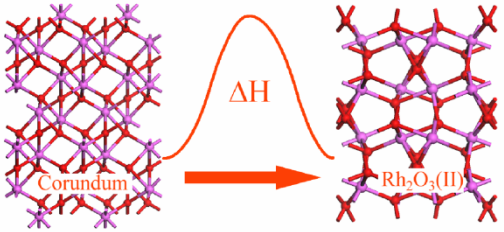








Elastic Properties

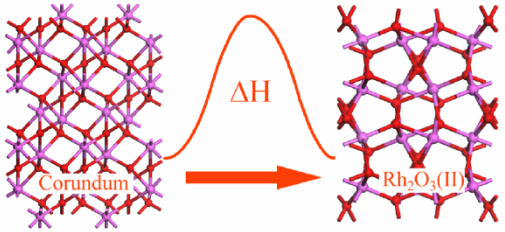


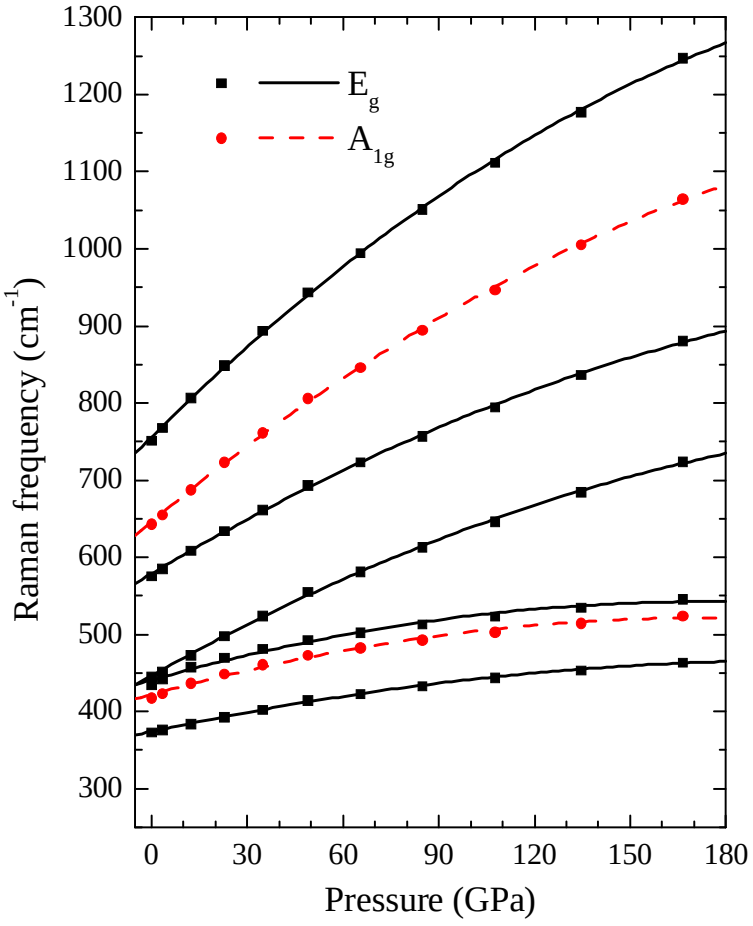
	84 GPa		160 GPa	
	Corundum	$Rh_2O_3(II)$	Corundum	$Rh_2O_3(II)$
C_{11}	956	976	1235	1288
C_{22}	844	851	1073	1085
C_{33}	852	1013	1213	1320
C_{12}	420	369	639	541
C_{13}	358	374	566	571
C_{23}	412	418	680	692
C_{44}	246	261	303	331
C_{55}	230	218	207	204
C_{66}	226	260	234	287
C_{15}	7	0	-5	0
C_{25}	19	0	10	0
C_{35}	21	0	24	0
C_{46}	-14	0	-25	0

- To compare the elasticity between the corundum and $Rh_2O_3(II)$ phase, The corundum phase is treated as the P2/c monoclinic structure with 20 atoms per unit cell.

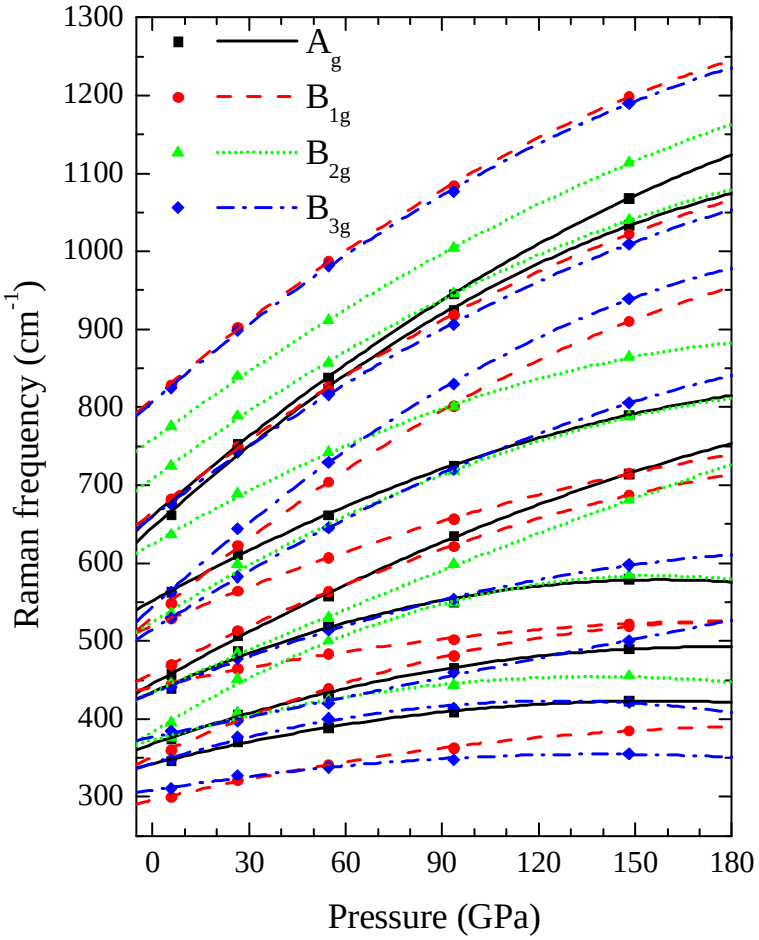
- From low pressure to high pressure, the elastic properties between corundum and $Rh_2O_3(II)$ phases are very comparable. The major differences are from C_{33} and C_{12}. The larger C_{33} of $Rh_2O_3(II)$ phase means that its c axis is less compressible than that of corundum.

Raman-Active Modes





Corundum Phase



Rh_2O_3(II) Phase

Thanks.

DOE (DE-FG02-03ER46060)

HRD-0317741 and EAR-0757847

Travel Scholarship