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Thermal Expansion of Periclase (MgO) and Tungsten (W) to Melting Temperatures

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Abstract *In situ* x-ray data on molar volumes of periclase and tungsten have been collected over the temperature range from 300 K to melting. We determine the temperature by combining the technique of spectroradiometry and electrical resistance wire heating. The thermal expansion (α) of periclase between 300 and 3100 K is given by $\alpha = 2.6025\ 10^{-5} + 1.3535\ 10^{-8}\,T + 6.5687\ 10^{-3}\,T^{-1} - 1.8281\,T^{-2}$.

For tungsten, we have (300 to 3600 K) $\alpha = 7.862\ 10^{-6} + 6.392\ 10^{-9}\,T$.

The data at 298 K for periclase is: molar volume 11.246 (0.031) cm^3, $\alpha = 3.15$ (0.07) $10^{-5}\,K^{-1}$, and for tungsten: molar volume 9.55 cm^3, $\alpha = 9.77$ (10.08) $10^{-6}\,K^{-1}$.

Introduction

Periclase (MgO) in solid solution with FeO is an important constituent of Earth's lower mantle. Tungsten (W) is an important industrial metal. It is also important in experimental mineral physics because its pressure-volume-temperature data can be used for *in situ* x-ray studies of heated solids under pressure with tungsten as a standard. In the past, equation of state for both these solids have been constructed from data over a limited temperature and pressure range (Saxena and Zhang 1990). In addition to experiments on measuring thermal expansion of periclase by many experimental groups (see, for example, Campbell 1962; Touloukian et al. 1977; Suzuki 1975; Hazen 1976) and tungsten by Kirby (1972) and Petukov and Chekovskoi (1972), data assessments have been made by Reeber et al. (1995) and Anderson (1995).

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Experimental Method

We obtained powder X-ray diffraction data with a Siemens x-ray system consisting of a Smart CCD Area Detector and a direct-drive rotating anode as x-ray generator (18 kW). MoK_α radiation (tube voltage 50 kV, tube current 24 mA, cathode gun 0.1×1 mm) monochromatized by using an incident beam graphite monochromator was passed through a collimator of diameter 200 μm to the sample. The diffracted x-ray was collected on a 512×512 pixels area detector. Data were acquired for different experiments at different fixed 2θ settings of 20 and 30° (corresponding to fixed positions of the detector) and by varying the sample-to-detector distance (120–260 mm). Settings of the detector were carefully calibrated using three independent standards (Pt, NaCl, Al_2O_3) at each position of the detector. Since a large portion of the Debye ring is measured on the detector surface, it reduces the counting time by the solid angle covered. This angular range also helps in collecting data that might be missed if linear detectors were used: the area under investigation may have substantial preferred orientation or may recrystallize (the sample cannot be rotated during heating). Usually data collection time is 10–30 s, but due to small size of our samples (see below), time of collection was 120 s and at high temperatures (>3000 K) up to 600 s.

We heat the sample electrically with a versatile heating cell (McMillan et al. 1994) (Fig. 1). The tungsten wire with a diameter of 0.35 mm was flattened in its center using the diamond anvil cell (DAC) with culet size of 0.6 mm. In the center of the flattened part, a hole of 0.125 mm diameter was drilled using erosion drill (BET-SA). Fine powder of the sample was put in the hole and pressurized using DAC to obtain flat clear surface. To avoid oxidation, the wire was heated in the cell with inert (Ar) atmosphere (Fig. 1). The W wire furnace was connected to 0–20V/0–20A power supply. Currents on the order of 15 A were sufficient to heat the wire to 3600 K. For each experiment, we used new wire and did not observe any change in power (or resistance of wire) during x-ray data collection time (maximum 600 s). For power-temperature calibration in the interval 1000 to 3600 K we used spectroradiometric thermometry (Hiernaut et al. 1989; Saxena and Dubrovinsky 1996). The gray body radiation of tungsten was measured in spectral range of 650–950 nm. The emissivity of tungsten is well-known (Cabannes 1967; Wall et al. 1992; Saxena and Dubrovinsky 1996) and the error in a temperature measurement at wavelength less than 950 nm according to Corwin ad Rodenburgh (1994) is less than 1%. Fig. 2 shows the example of the power-temperature calibration curve during heating and cooling of the wire. The error in temperature was within ±0.5% up to 3500 K.

We carried out several experiments by heating and cooling pure tungsten wire and tungsten wire with periclase in a hole in the wire. Unit cell parameters (Table 1) were calculated using reflec-

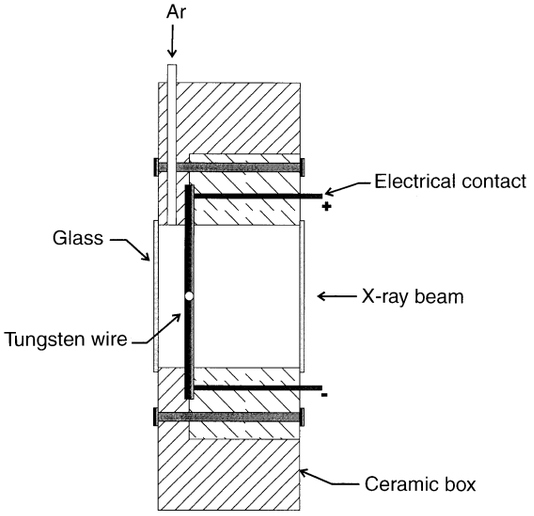

Fig. 1 Schematic diagram of the tungsten wire heating cell

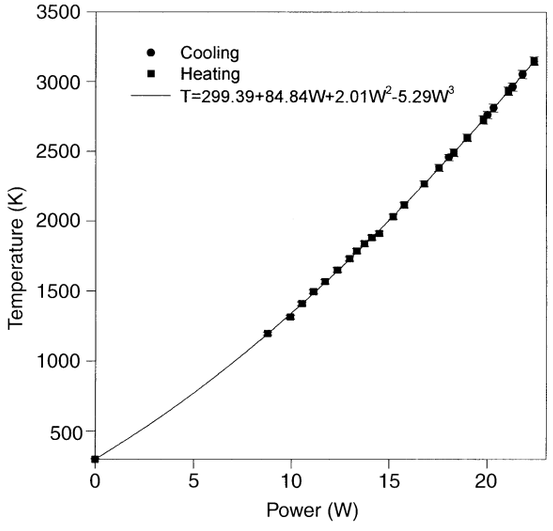

Fig. 2 Typical electric power and temperature calibration of the tungsten wire. The temperature is determined by the spectroradiometric method previously tested by melting a series of different solids (Saxena and Dubrovinsky 1996)

tions with indexes (110), (200), (112), (220), (310), (222) of tungsten and (111), (200), (220), (113), (222), (400) and (420) of periclase. At temperatures higher than 3200 K, we were able to observe only (110), (200), (112) and (310) reflections of tungsten and at temperature higher than 2700 K reflections (111), (200), (220) and (222) of periclase. The error in lattice parameters for both tungsten and periclase was less than 5 10^{-4} Å at medium temperatures (up to 2500 (4) K); it increases up to 5 $^{10-}$3 Å near melting points.

Table 1 Volume of periclase (MgO) and tungsten (W) as function of temperature

Temperature, K	Volume, cm^3/mole	Temperature, K	Volume, cm^3/mole
Periclase (MgO)		Tungsten, W	
1	2	1	2
298	11.2434(0.0090)	298	9.5462(0.0072)
455	11.3004(0.0054)	455	9.5679(0.0090)
710	11.4109(0.0136)	905	9.6216(0.0054)
905	11.5452(0.0118)	918	9.6277(0.0151)
1096	11.6211(0.0072)	1205	9.6618(0.0136)
1205	11.6938(0.0151)	1363	9.6878(0.0118)
1305	11.7250(0.0122)	1410	9.7047(0.0128)
1365	11.7523(0.0183)	1527	9.7180(0.0189)
1527	11.8218(0.0245)	1537	9.7059(0.0122)
1598	11.9081(0.0153)	1685	9.7449(0.0107)
1685	11.9656(0.0245)	1846	9.7882(0.0183)
1870	12.0459(0.0185)	1870	9.7831(0.0083)
1915	12.0900(0.0216)	2032	9.7997(0.0245)
2055	12.2001(0.0248)	2171	9.8186(0.0153)
2106	12.2287(0.0233)	2310	9.8489(0.0245)
2245	12.3299(0.0215)	2450	9.8923(0.0185)
2297	12.3780(0.0250)	2620	9.9412(0.0216)
2395	12.4401(0.0226)	2720	9.9554(0.0139)
2408	12.4487(0.0204)	2774	9.9754(0.0248)
2592	12.6010(0.0185)	2830	9.9929(0.0170)
2703	12.6887(0.0216)	2929	10.0212(0.0233)
2785	12.7520(0.0248)	3130	10.0721(0.0215)
2848	12.8013 (0.0233)	3190	10.0895(0.0203)
2912	12.8621(0.0215)	3316	10.1248(0.0250)
2986	12.9244(0.0250)	3470	10.1784(0.0226)
3031	12.9982(0.0185)	3548	10.2031(0.0204)
3065	13.2013(0.0204)	3430	10.1478(0.0139)
3086	13.2264(0.0268)	3220	10.0995(0.0082)
3040	13.1823(0.0233)	2986	10.0229(0.0107)
3015	12.9723(0.0250)	2785	9.9899(0.0189)
		2650	9.9602(0.0128)
		2592	9.9484(0.0118)
		2395	9.8817(0.0136)
		2245	9.8484(0.0094)
		2055	9.8182(0.0090)

Results and Discussion

Periclase

The melting temperature of periclase as determined by Kracek and Clark (1966) is 3068 (20) K. At a temperature of 3065 (30) K, we observed diffraction lines of periclase and, at 3110 (30) K they disappeared. After cooling down to 3086 (30) K, reflections (200) and (220) of periclase appear again. Hence, we measured the melting point of periclase as 3098 (42) K.

The molar volume of periclase to melting temperature (Table 1) is plotted against temperature in Fig. 3, the variation of thermal expansion (α) with temperature is shown in Fig. 4. We note that the data in Fig. 4 deviate only slightly from a straight line. The temperature dependence of α is found by fitting

$$V_{lbar,T}=V_0\left[\exp\left(\int_{298}^{T}\alpha dT\right)\right] \quad (1)$$

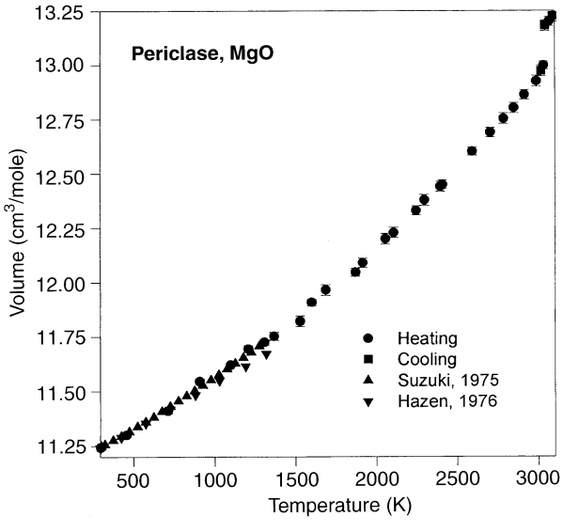

Fig. 3 Molar volume of periclase as a function of temperature. The data of this study is plotted along with those of Suzuki (1975) and Hazen (1976). The solid line is described by equation $V=11.246\ \exp\ (2.6025\ 10^{-5}\ (T-300)+6.7675\ 10^{-9}\ (T^2-90000+6.5687\ 10^{-3}\ \ln\ (T/300)+1.8281\ (1/T-3.3333\ 10^{-3}))$

to the molar volume-temperature data which gives

$$\alpha=2.6025\ (0.0633)\ 10^{-5}+1.3535\ (0.0162)\,10^{-8}\ T +6.5687\ (0.0688)\ 10^{-3}\ T^{-1} -1.8281\ (0.205)\ T^{-2} \quad (2)$$

(numbers in parentheses are standard deviations).

The V_0 at 298 K is 11.246 (0.030) cm^3.

An extrapolation to low temperature may be done following the method of Reeber et al. (1995). According to modified quasi-harmonic model (MQHM) (Reeber et al. 1995) lattice parameters of cubic crystals may be described by the following equation

$$a(T)=a_0\exp\left[\frac{X_1\theta_1}{\exp(\theta_1/T)-1}+\frac{X_2\theta_2}{\exp(\theta_2/T)-1} +\frac{X_3\theta_3}{\exp(\theta_3/T)-1}\right]+a_2(T-T_c)^2H(T,T_c), \quad (3)$$

where α_0 is the lattice parameter at 0 K, X_i and θ_i parameters of the MQHM model (i=1,2,3), α_2 and T_c coefficients which determine the influence of defects on thermal expansion, $H(T,T_c)$ a step function $(H(T,T_c)=0$ if $T<T_c$, $H(T,T_c)=1$ if $T\geq T_c$.

Results of fitting our experimental data with Eq. (3) are presented in Fig. 5 and in Table 2. The thermal expansion is quite close to that predicted by Reeber et al. (1995). The "kink" in both our curve and the curve of Reeber et al. (1995) showing the temperature dependence of thermal expansion at $T=T_c$ (Fig. 3) is due to the second term in Eq. (3) and, probably, do not have any physical meaning.

Saxena et al. (1993) on the basis of assessment of thermodynamic data suggested the following equation

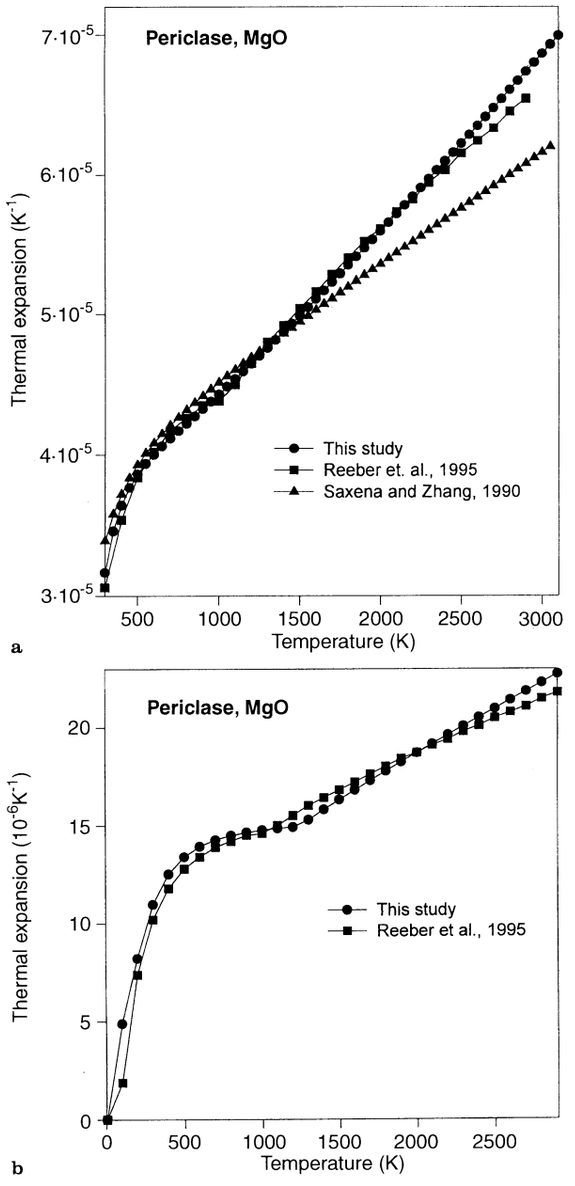

Fig. 4a, b Thermal expansion of periclase as a function of temperature given by Eq. (3) (**a**) and Eq. (4) (**b**). For most of the temperature range the curve follows the extrapolation by Reeber et al. (1995) well. There is a large deviation at high temperature from the Saxena and Zhang (1990) curve

for thermal expansion of periclase:

$$\alpha=3.64\ 10^{-5}+8.35\ 10^{-9}\ T +8.5\ 10^{-4}\ T^{-1}-0.95\ T^{-2}. \quad (4)$$

Since the temperature dependence of α at high temperatures is larger than that given by Saxena et al. (1993) (Fig. 4a), the data on temperature dependence of compressibility (Saxena et al. 1993) need adjustment and is

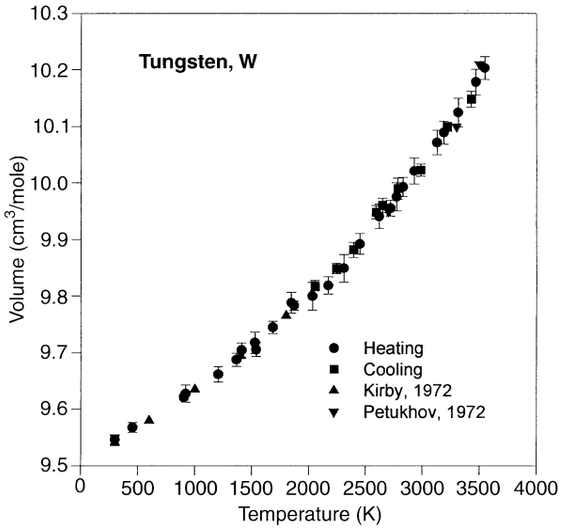

Fig. 5 Molar volume of tungsten as a function of temperature. The data of this study is consistent with two previous studies. The solid line is described by equation V=9.55 exp (7.862 10^{-6} (T-300)+6.392 10^{-9} (T^2-90000)). The thermal expansion varies quite linearly with temperature

Table 2 Modified quasi-harmonic model fitting parameters (Reeber et al. 1995) for periclase (MgO) and tungsten (W)

	Periclase (MgO)	Tungsten (W)
θ_1, K	80.91	2.505
θ_2, K	803.50	6.017
θ_3, K	755.85	1.906
X_1, 10^{-6} K	4.852	1.979
X_2, 10^{-6} K	4.026	0.529
X_3, 10^{-6} K	6.396	2.143
T_c, K	1233.05	1119.68
a^2, 10^{-8} A/K²	1.007	0.038
a_0 (0 K)	4.2028	3.1604

now given by

$$\beta\,(\mathrm{GPa}^{-1}) = 0.5668\ 10^{-6} + 9.8473\ 10^{-11}\ T + 3.2675\ 10^{-14}\ T^2 + 9.7895\ 10^{-18}\ T^3. \quad (5)$$

The bulk modulus (K_T) will be the inverse of β.

Note also that our new data on thermal expansion of periclase do not change conclusions made by Anderson (1995) that thermal pressure (the product αK_T) is practically independent of temperature (at least up to 1800 K at which experimental data on K_T are available).

Tungsten

The molar volume data on tungsten (Table 1) as a function of temperature is shown in Fig. 5. The data can be fitted with

$$\alpha = 7.862\ (0.080)\ 10^{-6} + 6.392\ (0.037)\ 10^{-9}\ T \quad (6)$$

and a molar volume of 9.550 (0.005) cm^3 at 298 K.

The result described our experimental data with MQHM (Eq. (3)) is presented in Table 2.

Saxena and Zhang (1990) suggested the following equation for thermal expansion of tungsten

$$\alpha = 9.386\ 10^{-6} + 5.51\ 10^{-9}\ T. \quad (7)$$

The comparison of α calculated by Eqs (6) and (7) shows that our new experimental data is again somewhat larger than given by Saxena and Zhang (1990). However, the new result does not require any change in the data on temperature dependence of bulk modulus given by Saxena and Zhang (1990).

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