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Thermoelastic equation of state of jadeite $NaAlSi_2O_6$: An energy-dispersive Reitveld refinement study of low symmetry and multiple phases diffraction

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Abstract. We report the first measurement of a complete set of thermoelastic equation of state of a clinopyroxene mineral. We have conducted an *in situ* synchrotron x-ray diffraction study of jadeite at simultaneous high pressures and high temperatures. A modified Rietveld profile refinement program has been applied to refine the diffraction spectra of low symmetry and multiple phases observed in energy dispersive mode. Unit cell volumes, measured up to 8.2 GPa and 1280 K, are fitted to a modified high-temperature Birch-Murnaghan equation of state. The derived thermoelastic parameters of the jadeite are: bulk modulus K=125 GPa with assumed pressure derivative of bulk modulus K' = $\partial K/\partial P = 5.0$, temperature derivative of bulk modulus $\dot{K} = \partial K/\partial T = -1.65\times10^{-2}$ GPa K^{-1}, and volumetric thermal expansivity $\alpha = a + bT$ with values of $a=2.56\times10^{-5}K^{-1}$ and $b=0.26\times10^{-8}$ K^{-2}. We also derived thermal Grüneisen parameter $\gamma_{th}=1.06$ for ambient conditions; Anderson-Grüneisen parameter $\delta_{To}=5.02$, and pressure derivative of thermal expansion $\partial\alpha/\partial P = -1.06\times10^{-6}$ K^{-1} GPa^{-1}. From the *P-V-T* data and the thermoelastic equation of state, thermal expansions at five constant pressures of 1.0, 2.5, 4.0, 5.5, and 7.5 GPa are calculated. The derived pressure dependence of thermal expansion is: $\Delta\alpha/\Delta P = -0.97\times10^{-6}K^{-1}GPa^{-1}$, in good agreement with the thermodynamic relations.

Introduction

Thermoelastic equations of state of the mantle minerals provide important constraints on the chemical composition of Earth's mantle (*Weidner and Ito*, 1987; *Duffy and Anderson*, 1989; *Zhao and Anderson*, 1994). Pyroxenes, the second most abundant minerals (after olivine), are of great importance in mineralogical models of the upper mantle (*Ringwood*, 1975, *Anderson and Bass*, 1984). Jadeite is a major component of the clinopyroxene minerals; it has a chemical composition $NaAlSi_2O_6$ and a monoclinic crystal structure of space group *C2/c*. Many physical properties of jadeite have been measured such as: thermal expansion (*Cameron et al.*, 1973), heat capacity (*Robie et al.*, 1978), and single-crystal elasticity (*Kandelin and Weidner*, 1988). However, the temperature derivatives of elastic moduli and the pressure derivative of thermal expansion, which are very important thermoelastic parameters for evaluating depth dependence of seismic properties (*D.L. Anderson*, 1988; *O.L. Anderson*, 1995), have never been investigated for the clinopyroxenes due to significant experimental difficulties.

This is the first experimental study to derive a complete set of thermoelastic parameters for a clinopyroxene mineral. We conducted an *in situ* synchrotron x-ray diffraction study on jadeite under conditions of simultaneous high pressure *P* and temperature *T* conditions. The energy-dispersive diffraction spectra were processed by a modified Rietveld profile refinement (*Rietveld*, 1969) program GSAS (*Larson and Von Dreele*, 1988). The unit cell dimensions of jadeite were measured as function of pressure and temperature. The observed *Pressure-Volume-Temperature* data were fitted with a modified high-temperature Birch-Murnaghan equation of state and a complete set of thermoelastic parameters of jadeite is thus derived. A tradeoff test was conducted to evaluate experimental accuracy and comparisons with previous experimental data are presented. The importance of the clinopyroxene minerals to mantle mineralogical modeling are also discussed.

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Experimental Aspects

High P-T Synchrotron X-ray Diffraction Study

High P-T *in-situ* X-ray diffraction was achieved by integrating a DIA-6 type multi-anvil press (SAM-85, Stony Brook) with a synchrotron white radiation source (Superconducting wiggler port X-17B, NSLS, Brookhaven National Lab.). Energy-dispersive spectra of the powder sample were collected with a Ge solid state detector at a fixed Bragg angle of $2\theta=5.847°$. Sample temperature was monitored with a Pt-Pt/10%Rh thermocouple and controlled by a DC power supply. The powder sample of jadeite $NaAlSi_2O_6$ (*Litvin and Gasparik*, 1993) was packed into half of a cylindrical hexagonal boron nitride *h*BN sample chamber 1 mm in diameter and 2 mm long. NaCl powder for pressure standard (*Decker*, 1971) was packed separately into the other half of the sample chamber. The cylindrical *h*BN sample chamber was placed in an amorphous carbon heater and embedded in a boron-epoxy cube to form the high *P-T* cell assembly.

Generally, significant deviatoric stress is applied in the sample at the initial "cold" compression stage (*Weidner et al.*, 1992; *Zhao et al.*, 1994), it decreases drastically upon heating and eventually vanishes as the temperature reaches about 800~1000 K. Thus, we first compress the cell assembly to the highest desired pressure and then heat the sample to the highest desired temperature. The stress field in the sample becomes pseudo-hydrostatic at high temperature and remains so for the succeeding cooling and decompression steps (*see* figure 3 in *Zhao et al.* 1996). Only those *P-V-T* data observed at hydrostatic compression conditions are used to derive the thermoelastic equation of state parameters.

Refinement of Diffraction Peaks and Cell Dimensions

Energy-dispersive diffraction spectra of the jadeite $NaAlSi_2O_6$ observed at high-pressures and high-temperatures have peak

widths about the same as at ambient conditions, a good indication of hydrostatic compression on the sample (*Zhao et al.*, 1994). Peak overlapping is a significant problem in the present study due to the low crystal symmetry (monoclinic C2/c) of jadeite and also because of the mixture of diffraction of *h*BN phase, coming from the sample chamber. Conventional peak-indexing and least-square refinement routine are no longer suitable for refinement of the complicated diffraction pattern of low symmetry and multiple phases.

We ran a Rietveld profile refinement (*Rietveld*, 1969) using a modified version of the General Structure Analysis System (GSAS, *Larson and Von Dreele*, 1988) for the energy-dispersive spectra. The peak positions and the lattice parameters of the whole-pattern diffraction spectra are refined simultaneously for multiple phases. Least-square fitting of the diffraction profile is achieved by minimization of the differences between the observed pattern and a synthetic pattern. Structure factors are extracted from the refinement of energy dispersive spectra using le Bail's technique (*le Bail*, 1988).

Shown in figure 1 is the result of a Rietveld refinement for an energy dispersive spectrum of jadeite $NaAlSi_2O_6$ and for hexagonal boron nitride *h*BN observed at a pressure of 6.88 GPa and temperature of 1280 K. The precision of the lattice parameters of NaCl is determined to be better than 0.3‰ in all refinement results. Accordingly, relative error in the pressure determination is about 0.08~0.12 GPa. The *Rietveld* profile refinement technique provides means for the determination of lattice parameters for the whole-pattern energy dispersive spectra. The speed and precision of the technique suggest that it is possible to quickly refine unit cell dimensions and structural/thermal parameters of the powder sample at simultaneous high pressure and high temperature conditions, even in complicated diffraction case of low-symmetry and multiple phases, (*Zhao et al.*, 1996).

Thermoelastic Equation of State

The Birch-Murnaghan equation of state (*Birch*, 1947) has often been used to fit isothermal compression data. A modified high-temperature Birch-Murnaghan equation of state is applied to fit the *P-V-T* data so as to cover a variable temperature range. It is important to indicate that, when fitting the equation of state parameters, any *V(P,T)* data point should be reached by taking a realistic thermodynamic path. A standard way to fulfill the thermodynamic necessity is to heat the ambient volume V_o to a "foot" temperature T and then compress the expanded volume *V(0,T)* along an isotherm to reach the *V(P,T)*. The modified Birch-Murnaghan equation of state (truncated at third order) for high temperatures is written as:

$$P = 3K_T f(1+2f)^{5/2}\left[1 - \frac{3}{2}(4-K')f + \ldots\right] \qquad (1)$$

where $K_T = K_{T_o} + \dot{K}(T-300)$

$K' = \partial K/\partial P$, $\dot{K} = \partial K/\partial T$

and $f = \frac{1}{2}[(V_T/V_{PT})^{2/3} - 1]$

$V_T = V_o \exp(\int \alpha(0,T)dT)$

where V_o is the cell volume at ambient conditions, V_T=*V(0,T)* at high-*T*, V_{PT}=*V(P,T)* at simultaneous high *P-T* conditions; volumetric thermal expansion at the atmospheric pressure $\alpha = \alpha(0,T) = a + bT - c/T^2$ (*T* in Kelvin, *see Suzuki*, 1975). We ignore the c/T^2 term in thermal expansion and high-order derivatives of the bulk modulus K'', $\ddot{K}$, and $\partial^2K/\partial P\partial T$ due to the limited *P-V-T* data range. Equation (1) modifies the isothermal Birch-Murnaghan equation of state by replacing K_o with K_T and substituting V_o/V_P with V_T/V_{PT} so that the temperature effects are accounted for.

Thermoelastic parameters for jadeite $NaAlSi_2O_6$ are derived by fitting the *P-V-T* data (Table 1) to the high-T Birch-Murnaghan equation of state (*eq.*1): isothermal bulk modulus K_{To}=124.5(4.0) GPa with an assumed pressure derivative of bulk modulus $K'=\partial K/\partial P=5.0$, temperature derivative of bulk modulus $\dot{K} = \partial K/\partial T = -1.65(49)\times10^{-2}$ GPa/K, volumetric thermal expansivity $\alpha = a + bT$ with values of a=2.56(22)x10^{-5}K^{-1} and b=0.26(18)x10^{-8} K^{-2}. Figure 2 shows the cell volumes against

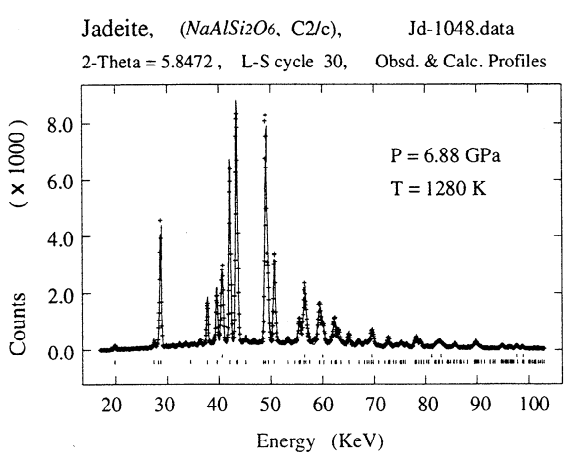

Figure 1. The refinement of powder x-ray diffraction pattern of jadeite. Observed energy dispersive data are indicated by cross "+"; the calculated pattern is drawn as a continuous line. Goodness of the fit is χ^2=6.5 with a residual of R_p=0.16. Bragg reflection positions are shown by short vertical bars marked below the diffraction pattern. Upper markers are for peaks of *h*BN, and lower markers are for jadeite. Notice there are some severe peak overlaps in the diffraction spectrum.

Table 1. Cell Dimensions of Jadeite at High *P-T* Conditions

P (GPa)	T (K)	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	V (Å^3)
0.00	300	9.401(1)	8.540(1)	5.268(1)	107.51(1)	403.32(8)
8.16	1280	9.272(1)	8.453(1)	5.182(2)	106.95(1)	388.54(9)
7.83	1072	9.268(1)	8.445(1)	5.183(2)	106.90(1)	388.12(9)
7.44	874	9.264(1)	8.437(1)	5.184(2)	106.94(1)	387.59(9)
7.02	670	9.258(1)	8.429(1)	5.181(2)	106.93(1)	386.79(9)
6.65	473	9.250(1)	8.421(1)	5.178(2)	106.94(1)	385.80(9)
6.33	308	9.244(1)	8.417(1)	5.179(2)	106.95(1)	385.41(9)
6.88	1280	9.315(1)	8.473(1)	5.198(2)	107.03(1)	392.23(9)
6.20	1072	9.303(1)	8.476(1)	5.197(2)	107.02(1)	391.85(9)
5.78	872	9.298(1)	8.460(1)	5.198(2)	107.04(1)	390.93(9)
5.50	672	9.292(1)	8.451(1)	5.199(2)	107.05(1)	390.28(9)
5.04	471	9.287(1)	8.443(1)	5.197(2)	107.06(1)	389.57(9)
4.73	307	9.284(1)	8.438(1)	5.195(2)	107.07(1)	389.06(9)
5.03	1278	9.369(1)	8.525(1)	5.207(2)	107.04(1)	397.06(9)
4.59	1072	9.342(1)	8.518(1)	5.213(1)	107.15(1)	396.36(6)
4.23	872	9.339(1)	8.507(1)	5.209(2)	107.10(1)	395.49(9)
3.88	673	9.336(1)	8.497(1)	5.205(2)	107.09(1)	394.69(9)
3.47	472	9.331(1)	8.485(1)	5.205(2)	107.13(1)	393.77(9)
3.17	307	9.325(1)	8.485(1)	5.204(2)	107.11(1)	393.16(9)
3.63	1276	9.387(1)	8.542(2)	5.243(1)	107.26(1)	401.46(8)
3.24	1073	9.377(1)	8.542(1)	5.236(2)	107.24(1)	400.53(9)
2.88	873	9.373(1)	8.531(1)	5.238(2)	107.23(1)	400.05(9)
2.48	672	9.369(1)	8.524(1)	5.233(2)	107.20(1)	399.20(9)
2.12	471	9.363(1)	8.520(1)	5.229(2)	107.17(1)	398.51(9)
1.77	308	9.354(1)	8.509(1)	5.232(1)	107.22(1)	397.76(5)
2.17	1275	9.443(1)	8.561(1)	5.275(1)	107.52(1)	406.70(6)
1.68	1073	9.438(1)	8.556(2)	5.271(1)	107.49(1)	405.97(7)
1.36	873	9.423(1)	8.560(1)	5.265(1)	107.43(1)	405.12(9)
0.95	671	9.417(1)	8.526(1)	5.277(1)	107.50(1)	404.08(6)
0.61	473	9.411(1)	8.521(1)	5.269(1)	107.41(1)	403.15(7)
0.41	308	9.403(1)	8.497(2)	5.281(1)	107.70(1)	401.94(9)

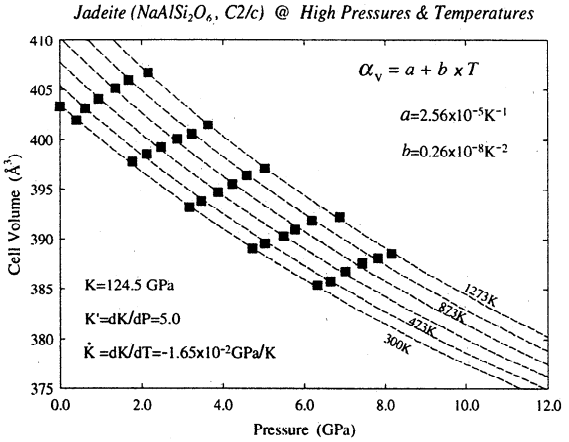

Figure 2. Cell volumes $V(P,T)$ of the jadeite $NaAlSi_2O_6$ against pressure. The curves represent isothermal compressions calculated from the fitted thermoelastic parameters. The isotherms are at temperature steps ΔT=200 K above 300 K and up to 1273 K. The observation errors are smaller than the symboles.

pressure. The isothermal compression lines calculated from the fitted thermoelastic parameters are also illustrated on the diagram. It is clear that the thermoelastic parameters derived in the present study produce good fits to the *P-V-T* data of jadeite.

Discussion

Thermoelastic equation of state parameters derived from *P-V-T* data and Equation (1) depend very much on the constraints imposed on the fitting procedure. It would be better to have independent compression data at room temperature and thermal expansion at atmospheric pressure. In the case of jadeite, thermal expansion α_o and adiabatic bulk modulus K_s have already been measured (*Cameron et al.*, 1973; *Kandelin and Weidner*, 1988). Thus, errors in determining of thermoelasticities are mostly from inaccuracy of K′ and V_o. We performed a tradeoff test by fixing V_o=403 Å^3 and constraining K′ to be 4, 5, 6, respectively, and results are listed in Table 2:

Table 2. Tradeoffs in fitting thermoelastic E.O.S. of jadeite

	K′=4.0	K′=5.0	K′=6.0	K′=9.7(9)
a (10^{-5} K^{-1})	2.51(23)	2.56(22)	2.62(21)	2.91(17)
b (10^{-8} K^{-2})	0.24(19)	0.26(18)	0.29(18)	0.25(15)
K_{To} (GPa)	127(5)	125(4)	122(4)	114(5)
$\dot{K}$ (-10^{-2}GPaK^{-1})	1.40(51)	1.65(49)	1.89(48)	2.53(37)

For the last column, we did not impose constraint on K′ and the derived α_{vo} and K_{To} are farther away from previous experimental results. The pressure range in present study is not large enough to resolve the K′ confidently. Further experiments would better refine the thermoelastic E.O.S. of jadeite.

Thermal Grüneisen parameter at ambient conditions can be derived from the refined thermoelastic data with the formula:

$$\gamma_{th} = \frac{\alpha_v \cdot K_T}{\rho \cdot C_v} \qquad (2)$$

We have α_{vo} =2.64×10^{-5} K^{-1} , K_{To}=124.5 GPa, ρ_o=3.33 g/cm^3 plus isochoric heat capacity C_v=92.8 J/mol/K from *Kieffer* (1980). The derived thermal Grüneisen parameter of jadeite is: γ_{th} =1.06 for ambient conditions.

Anderson-Grüneisen parameter, a widely applied parameter in Earth mantle modeling, is directly related to the temperature derivative of bulk modulus:

$$\delta_T = -\frac{1}{\alpha_v K_T}\left(\frac{\partial K_T}{\partial T}\right)_P \qquad (3)$$

At ambient conditions, α_{vo}=2.64×10^{-5} K^{-1} , K_{To}=124.5 GPa, and $\partial K/\partial T$ = -1.65×10^{-2} GPa/K. Thus, the jadeite Anderson-Grüneisen parameter is calculated to be: δ_{To}≈5.02.

The change of thermal expansion with pressure is directly related to the change of bulk modulus with temperature. Through the thermodynamic identity:

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = \frac{1}{K_T^2}\left(\frac{\partial K_T}{\partial T}\right)_P \qquad (4)$$

and using the derived thermoelastic parameters, the pressure derivative of thermal expansion for the jadeite is calculated to be: $\partial\alpha/\partial P$= -1.06×10^{-6}K^{-1}GPa^{-1}.

The pressure derivative of thermal expansion may also be explored with a different approach. Plotted in figure 3 are cell volumes against temperatures. The raw experimental *P-V-T* data, as shown by the empty circles, are pretty much lined up in the diagram, although with different pressures. One may correct the raw $V(P,T)$ data to certain constant pressures P_cs to get the volume $V(P_c,T)$ using the high-T Birch-Murnaghan equation of state.

The track of this correction is to back-derive $V(0,T)$ from $V(P,T)$ first and then compress $V(0,T)$ to $V(P_c,T)$. Again, we use the derived thermoelastic parameters: K_{To}=124.5 GPa; K'=5.0; and $\dot{K}$ = -1.65×10^{-2} GPa K^{-1}. The solid diamond symbols plotted in the figure 3 are the corrected $V(P_c,T)$ data for five P_cs. The thermal expansions at these five constant pressures can thus be traced out in the $V(P_c)$-T plot with straight-line regressions. For the temperature range 300~1300 K, the fitted values $\alpha_v(P_c)$ are: 2.70, 2.61, 2.47, 2.28, and 2.12 ×10^{-5} K^{-1} for P_cs of 1.0, 2.5, 4.0, 5.5, and 7.5 GPa, respectively.

We plot the five fitted thermal expansions against pressure in figure 4 and a linear equation: $\alpha=\alpha_o+(\Delta\alpha/\Delta P)\,P$ is applied for data regression. The fitted slope of the straight line is the pressure derivative of thermal expansion: $\Delta\alpha/\Delta P$ = -0.97(5)×10^{-6} K^{-1} GPa^{-1}. It is quite close to the value $\partial\alpha/\partial P$ = -1.06×10^{-6} K^{-1} GPa^{-1} derived from the approach of thermodynamic identity (*eq.*

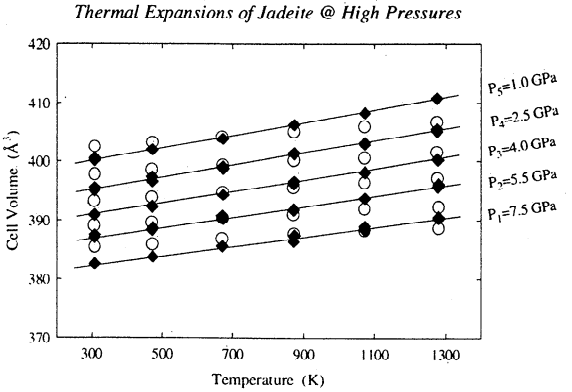

Figure 3. The cell volumes $V(P,T)$ of jadeite $NaAlSi_2O_6$ against temperature. The circles represent the raw *P-V-T* data while solid diamonds are the corrected cell volumes $V(P_c,T)$ for P_cs of 1.0, 2.5, 4.0, 5.5, and 7.5 GPa, respectively. Data points in between any two P_cs are corrected twice to both P_cs, (Vol. up and down corresponds to decompression and compression, respectively). Five straight lines are fitted for thermal expansions at five P_c s, respectively.

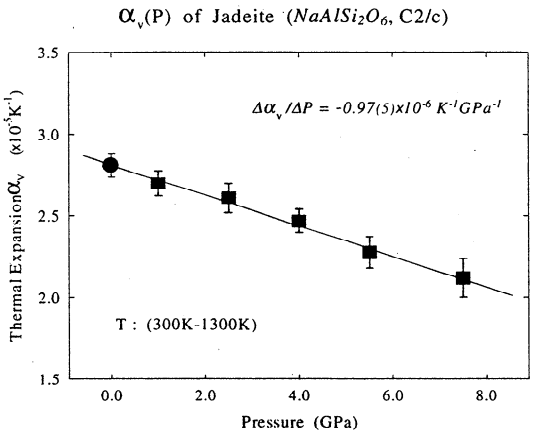

Figure 4. Thermal expansions of jadeite $NaAlSi_2O_6$ plotted as a function of pressure. The slope of the fitted straight line represents pressure derivative of thermal expansion, $\Delta\alpha/\Delta P$. Solid circle is the regression result for thermal expansion at atmospheric pressure α_0.

4). Thermal expansion at atmospheric pressure can also be derived by the straight line regression: $\alpha_0=2.81(7)\times10^{-5}$ K^{-1} for T=300-1300 K. The errors reported here are only for the straight-line fits in Figure 3 and they could be larger because of error propagation through the pressure correction procedures, where many fitted thermoelastic parameters are employed.

Conclusion

High P-T *in-situ* x-ray diffraction experiment provides the means for determining the thermoelastic equation of state of mantle minerals. Using Rietveld refinement, we are able to refine peak positions and lattice parameters simultaneously for the diffraction spectra observed in energy dispersive mode. Jadeite $NaAlSi_2O_6$, is a major sodium- and aluminum- bearing mineral. Its thermodynamic properties are important to the understanding of phase relation of enstatite-jadeite-diopside join in the upper mantle. Thermoelastic parameters of the clinopyroxenes are essential for the modeling of seismic profile and discontinuity at the top of transition zone related to pyroxene to garnet transition. We have measured unit cell parameters for jadeite for pressure up to 8.2 GPa and temperature up to 1280 K. These observations greatly extend our knowledge of pyroxene structure by mapping a corresponding volume in P-V-T space. With these information we can derive a complete set of internally consistent thermoelastic parameters for this material. We note that thermoelastic parameters of jadeite $NaAlSi_2O_6$ (mean atomic mass $\overline{m}$ =20.2g) are quite different from that of orthoenstatite $MgSiO_3$ ($\overline{m}$ =20.1g). The thermal expansion and compression of jadeite are about 78% and 82% of the value of orthoenstatite, respectively (see *Zhao et al.*, 1995). The pressure and temperature derivatives, namely $\partial\alpha/\partial P$ and $\partial K/\partial T$, of jadeite are only accounted for 30% and 44% of the value for orthoenstatite. We consider that crystal structure (clino- *vs.* ortho-) plays an important role in determining the volume change with pressure and temperature, resulting thus in significant differences in thermoelastic parameters of these two minerals. A complete set of thermoelastic equations of state for clinopyroxene minerals can be determined by applying the direct and precise experimental and refinement techniques presented in this study. This approach is very much needed in order to conduct the modeling of composition and dynamics of the Earth's mantle.

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