Thermoelastic equation of state of jadeite NaAlSi$_2$O$_6$: 
An energy-dispersive Rietveld refinement study of 
low symmetry and multiple phases diffraction

Yusheng Zhao, Robert B. Von Dreele, Thomas J. Shankland
Los Alamos National Laboratory, Los Alamos, New Mexico

Donald J. Weidner, Jianzhong Zhang, Yanbin Wang, Tibor Gasparik
State University of New York at Stony Brook, Stony Brook, New York

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 $\beta = \frac{\partial K}{\partial P} = 5.0$, temperature derivative of bulk modulus $\alpha = \frac{\partial K}{\partial T} = -1.65 \times 10^2$ GPa$^{-1}$, and volumetric thermal expansivity $\alpha_v = \alpha + \beta T$ with values of $a = 2.56 \times 10^{-4}$ K$^{-1}$ and $b = 0.26 \times 10^{-8}$ K$^{-2}$. We also 
 derived thermal Grüneisen parameter $\gamma_t = 1.06$ for ambient 
 conditions, Anderson-Grüneisen parameter $\delta = 5.02$, and 
 pressure derivative of thermal expansion $\partial \alpha_v / \partial P = -1.06 \times 10^8$ 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 $\Delta \alpha / \Delta P = -0.97 \times 10^{-4}$ 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 Ino, 1987; Duffy and Anderson, 1989; Thau 
 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$_2$O$_6$ 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 (Kandel 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.

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 2θ = 5.847°. Sample temperature 
 was monitored with a Pt-Pt10%Rh thermocouple and controlled 
 by a DC power supply. The powder sample of jadeite NaAlSi$_2$O$_6$ 
 (Litvin and Gasparik, 1993) was packed into half of a cylindrical 
 hexagonal boron nitride hBN 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 hBN 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$_2$O$_6$ 
 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 deformation of hBN phase, coming from the sample chamber. Conventional peak-indexing and least-square refinement routines 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 and 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 NaAlSi2O6 and for hexagonal boron nitride hBN 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 0.5% 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 isostructural 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 variety temperature range. It is important to indicate that, when fitting the equation of state parameters, any P(V,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 V0 to a “foot” temperature T and then compress the expanded volume V(T,T) along an isotherm to reach the W(P,T). The modified Birch-Murnaghan equation of state (truncated at third order) for high temperatures is written as:

\[
P = 3 K_T f(1+2f)^{\frac{2}{3}} \left[ 1 - \frac{3}{2} (4K^*-f) f + ... \right]
\]

where

\[
K_T = K_T^{0} + \dot{K}(T - 300)
\]

\[
\dot{K} = \frac{K^*}{\dot{\theta}^*} \quad \dot{\theta} = \frac{\partial P}{\partial T}
\]

and

\[
f = \frac{1}{2} (V / V_T)^{\frac{3}{2}} + 1
\]

where V is the cell volume at ambient conditions, V_T=V(0,T) at high-T, V_P=V(P,T) at simultaneous high P-T conditions; volumetric thermal expansion at the atmospheric pressure \(\alpha = \alpha (0,T) = a + bT + cT^2\) (T in Kelvin, see Suzuki, 1975). We ignore the \(cT^2\) term in thermal expansion and high-order derivatives of the bulk modulus \(K^*\), \(K\), and \(\partial K/\partial T\) due to the limited P-T data range. Equation (1) modifies the isothermal Birch-Murnaghan equation of state by replacing \(K_0\) with \(K_T\) and substituting \(V_P V_T\) with \(V_P V_T\) so that the temperature effects are accounted for.

Thermoelastic parameters for jadeite NaAlSi2O6 are derived by fitting the P-V-T data (Table 1) to the high-T Birch-Murnaghan equation of state (eq.1) with an assumed pressure derivative of bulk modulus \(K = 2\dot{K}/\partial P = 5.0\), temperature derivative of bulk modulus \(K = \dot{K}/\partial T = -1.65(49) \times 10^{-4} \text{ GPa/K}\), volumetric thermal expansivity \(\alpha = a + bT\) with values of \(a = 2.56(22) \times 10^{-2} \text{ K}^{-1}\) and \(b = 0.26(18) \times 10^{-3} \text{ K}^2\). Figure 2 shows the cell volumes against

<table>
<thead>
<tr>
<th>Table 1. Cell Dimensions of Jadeite at High P-T Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (GPa)</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>0.00</td>
</tr>
<tr>
<td>0.01</td>
</tr>
<tr>
<td>0.25</td>
</tr>
<tr>
<td>0.50</td>
</tr>
<tr>
<td>0.75</td>
</tr>
<tr>
<td>1.00</td>
</tr>
</tbody>
</table>

**Figure 1.** The refinement of powder x-ray diffraction pattern of jadeite. Observed energy dispersive data are indicated by cross "x"; the calculated pattern is drawn as a continuous line. Goodness of the fit is \(\chi^2=6.5\) 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 hBN, and lower markers are for jadeite. Notice there are some severe peak overlaps in the diffraction spectrum.
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 was better to have independent compression data at room temperature and thermal expansion at atmospheric pressure. In the case of jadeite, thermal expansion α and adiabatic bulk modulus K, have already been measured (Cameron et al., 1973; Kandel and Weidner, 1988). Thus, errors in determining of thermoelasticities are mostly from inaccuracy of K' and V_c. We performed a tracodoff test by fixing V_c=403 Å^3 and constraining K' to be 4, 5, 6, respectively, and results are listed in Table 2:

**Table 2.** Tracodoffs in fitting thermoelastic E.O.S. of jadeite

<table>
<thead>
<tr>
<th>K' = 4.0</th>
<th>K' = 5.0</th>
<th>K' = 6.0</th>
<th>K' = 9.7(9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (10^3 K^-1)</td>
<td>2.51(23)</td>
<td>2.56(22)</td>
<td>2.62(21)</td>
</tr>
<tr>
<td>b (10^3 K^-2)</td>
<td>0.24(19)</td>
<td>0.26(18)</td>
<td>0.26(18)</td>
</tr>
<tr>
<td>K_T (GPa)</td>
<td>12(3)</td>
<td>12(4)</td>
<td>12(4)</td>
</tr>
<tr>
<td>K'(-10^3 GPaK^-1)</td>
<td>1.40(51)</td>
<td>1.63(49)</td>
<td>1.69(48)</td>
</tr>
</tbody>
</table>

For the last column, we did not impose constraint on K' and the derived α_0 and K_T 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 F.O.S of jadeite.

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

\[ \gamma = \frac{\alpha_0}{\rho_C} K_T \]  

We have α_0 = 2.64×10^{-3} K^{-1}, K_T = 174.5 GPa, ρ_C = 3.33 g/cm^3 plus isotheric heat capacity C_v = 92.8 J/mol/K from Kieffer (1980). The derived thermal Grüniesen parameter of jadeite is: \[ \gamma = 1.06 \] for ambient conditions.

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

\[ \delta = \frac{\alpha_0}{K_T} \left( \frac{\partial K}{\partial T} \right) \tag{3} \]

At ambient conditions, α_0=2.64×10^{-3} K^{-1}, K_T=124.5 GPa, and \( \frac{\partial K}{\partial T} = -1.65×10^2 \) GPa/K. Thus, the jadeite Anderson-Grüniesen parameter is calculated to be: δ=1.502.

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

\[ \frac{\partial K}{\partial P} = \frac{1}{K_T} \left( \frac{\partial K}{\partial T} \right) \tag{4} \]

and using the derived thermoelastic parameters, the pressure derivative of thermal expansion for the jadeite is calculated to be: \( \frac{\partial \alpha}{\partial P} = -1.06×10^{-4} \) 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_s to get the volume V(P,T) using the high-T Birch-Murnaghian equation of state.

The track of this correction is to back-derive V(0,T) from V(P,T) and first compress V(0,T) to V(P,T). Again, we use the derived thermoelastic parameters: K_T=124.5 GPa; K' = 5.0, and K = 1.65×10^2 GPa K^{-1}. The solid diamond symbols plotted in figure 3 are the corrected V(P_s,T) data for five P_s. The thermal expansions at these five constant pressures can thus be traced out in the V(P_s,T) plot with straight-line regressions. For the temperature range 300–1300 K, the fitted values of α_0(P)_0 are: 2.70, 2.61, 2.47, 2.28, and 2.12×10^{-3} K^{-1} for P_s 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: α=α_0+(Δα/ΔP) P is applied for data regression. The fitted slope of the straight line is the pressure derivative of thermal expansion: \( \Delta \alpha / \Delta P = -0.97 (5)×10^{-4} \) K^{-1} GPa^{-1}. It is quite close to the value \( \Delta \alpha / \Delta P = -1.06×10^{-4} \) K^{-1} GPa^{-1} derived from the approach of thermodynamic identity (eq.}
4). Thermal expansion at atmospheric pressure can also be derived by the straight line regression: $\alpha_0 = 2.81(7) \times 10^{-6} \, K^{-1}$ 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 $M=20.2g$) are quite different from that of orthoenstatite $MgSiO_3$ ($M=20.1g$). 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 $d\alpha/dP$ and $dK/dT$, 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.

**Acknowledgments:** We thank Dr. I. Martinez and D.G. Isaak for constructive review of the manuscript. This work was supported by Institute of Geophysics and Planetary Physics and laboratory-directed research and development funding at Los Alamos. The SAM-85/NSLS project was supported by the NSF grant for the Center for High Pressure Research (CHPR), EAS-8920239.

**References**


Decker, D. L., High pressure equation of state for NaMgSi_2O_6 and CaMgSi_2O_6, J. Appl. Phys., 42, 3239-3244, 1971.


Yusheng Zhao, LANSCE, MS-H805, Los Alamos National Laboratory Los Alamos, NM 87545, U.S.A. (e-mail: yzhao@lanl.gov)

(Received: Mar. 28, 1996; Revised: Aug. 21, 1996; Accepted: Oct. 5, 1996)