

Thermoelastic Equation of State of Monoclinic Pyroxene: $\text{CaMgSi}_2\text{O}_6$ Diopside

Yusheng Zhao, R. B. Von Dreele, J. Z. Zhang*, and D. J. Weidner*

LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

* CHiPR, State University of New York at Stony Brook, Stony Brook, NY 11794, USA

We have conducted an *in situ* synchrotron x-ray diffraction study on a monoclinic pyroxene: $\text{CaMgSi}_2\text{O}_6$ diopside at simultaneous high pressures and high temperatures up to 8.2 GPa and 1280 K. 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. Thermoelastic parameters for diopside $\text{CaMgSi}_2\text{O}_6$ are derived by fitting the P - V - T data to the high- T Birch-Murnaghan equation of state. We obtained isothermal bulk modulus $K_{T0}=109.1$ GPa with a pressure derivative of bulk modulus $K'=\partial K/\partial P=4.84$, temperature derivative of bulk modulus $\dot{K}=\partial K/\partial T=-2.05 \times 10^{-2}$ GPa/K, volumetric thermal expansivity $\alpha=a+bT$ with values of $a=2.32 \times 10^{-5} \text{K}^{-1}$ and $b=1.88 \times 10^{-8} \text{K}^{-2}$.

[clinopyroxene, thermoelasticity, Rietveld refinement]

1. Introduction

Diopside is a major component of clinopyroxene minerals; it has a chemical composition $\text{CaMgSi}_2\text{O}_6$ and a monoclinic crystal structure with space group $C2/c$. Pyroxenes, the second most abundant minerals (after olivine), are of great importance in mineralogical models of the upper mantle. Thermoelastic equations of state of these mantle minerals provide important constraints on the chemical composition of Earth's deep interior^[1]. *In-situ* diffraction studies at simultaneous high pressures and temperatures are essential to obtain P - V - T data and to further derive the temperature derivatives of elastic moduli and the pressure derivative of thermal expansion. These thermoelastic parameters are important for evaluating depth dependence of seismic properties for the Earth's upper mantle and transition zone. However, clinopyroxenes have not been studied to much extent due to significant experimental difficulties associated with low crystal symmetry.

In present study, we describe a new experimental methodology to deal with low symmetry and multiple phases and applied it to derive P - V - T data for a clinopyroxene mineral. The energy-dispersive diffraction spectra observed in the high P - T synchrotron x-ray diffraction experiment were processed by a modified Rietveld refinement [2] program GSAS [3]. The unit cell dimensions of diopside $\text{CaMgSi}_2\text{O}_6$ were determined as functions 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 diopside is thus derived. An error analysis was conducted to evaluate experimental accuracy and comparisons with previous experimental data are also presented.

2. High P - T Experiment and Data Processing

A DIA-6 type multi-anvil press (SAM-85, Stony Brook) with a synchrotron white radiation source (X-17B, NSLS, Brookhaven) was used to conduct the high P - T *in-situ* X-ray diffraction experiments. Energy-dispersive spectra of the powder sample were collected with a Ge solid state detector at a fixed Bragg angle of $2\theta=5.847^\circ$. The sample temperature was monitored with a W-26%Rh/W thermocouple and controlled by a DC power supply. The powder sample of diopside $\text{CaMgSi}_2\text{O}_6$ was layer packed with NaCl powder, which served as the

pressure standard [4]. The cell assembly was first compressed to the highest desired pressure and then the sample was heated to the highest desired temperature. This procedure ensured that stress field in the sample became pseudo-hydrostatic at high temperature and remained so for the succeeding cooling and decompression steps. Only those P - V - T data observed at hydrostatic compression conditions are used to derive the thermoelastic equation of state parameters.

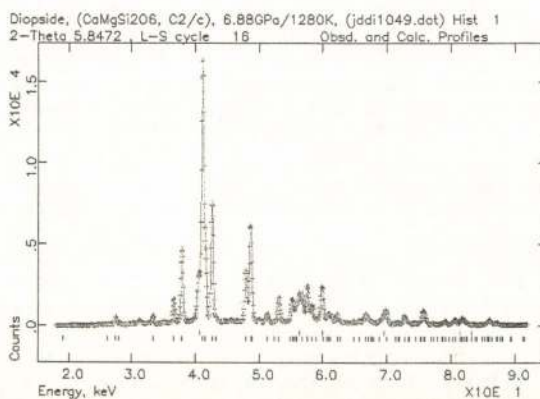


Fig 1. The Rietveld refinement of powder x-ray diffraction pattern of diopside. Observed energy dispersive data are indicated by cross "+"; the calculated pattern is drawn as a continuous line. Goodness of the fit is $\chi^2=5.4$ with a residual of $R_p=0.14$. Bragg reflection positions are shown by short vertical bars marked below the diffraction pattern. Upper markers are for peaks of *hBN* (sample chamber), and lower markers are for diopside. Notice severe peak overlaps in the diffraction spectrum due to low monoclinic symmetry and multiple phases.

Energy-dispersive diffraction spectra of the diopside $\text{CaMgSi}_2\text{O}_6$ 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 [5,6]. Peak overlap is a significant problem in the present study due to the low crystal symmetry (monoclinic $C2/c$) of diopside and also because of the additional diffraction lines from the *hBN* phase, coming from the sample chamber. Conventional peak-indexing and least-square refinement routines are not suitable for refinement of these complicated diffraction patterns of low

volumes against 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 diopside.

Discussion and Conclusion

The derived isothermal bulk modulus of 109(4) GPa is in good agreement with previously observed value of 113(3) GPa for the diopside. However, in the temperature range of 300-1300K, the derived thermal expansion of $\alpha_v = 3.82(8) \times 10^{-5} \text{ K}^{-1}$ is about 15% larger than the thermal expansion observed for single crystal diopside, of which only three data points were observed at high temperatures. 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_c s to get $V(P_c, T)$ using high-T Birch-Murnaghan equation of state.

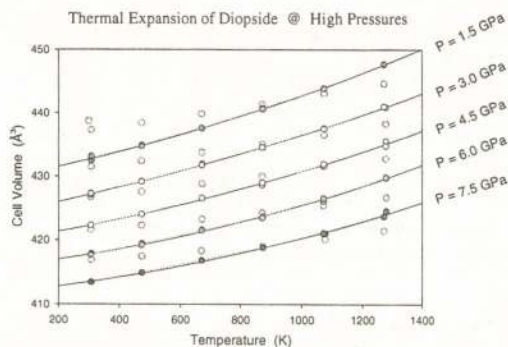


Fig 3. The cell volumes $V(P, T)$ of diopside $\text{CaMgSi}_2\text{O}_6$ against temperature. The empty circles represent the raw P - V - T data while filled solid symbols are the corrected cell volumes $V(P_c, T)$ for P_c s of 1.5, 3.0, 4.5, 6.0, and 7.5 GPa, respectively. Data points in between any two P_c s are corrected twice to both P_c s. (Volume up and down corresponds to decompression and compression, respectively).

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: $K_{T0} = 109$ GPa; $K' = 4.85$; and $K = -2.06 \times 10^{-2} \text{ GPa K}^{-1}$. The solid symbols plotted in the figure 3 are the corrected $V(P_c, T)$ data for five P_c s. The thermal expansions at these five constant pressures can thus be traced out in the $V(P_c, T)$ - T plot with a second order linear regressions of $V = b_0 + b_1 T + b_2 T^2$. Thus, the thermal expansion $\alpha = a + bT$ has the value $a = (b_1/b_2)$ and $b = (2b_2/b_2)$. We plot the six averaged thermal expansions for temperature range of 300K-1300K against pressure in figure 4. It is very clearly shown that the volumetric thermal expansion of the diopside decreases linearly with increasing pressure. The fitted slope of the straight line is the pressure derivative of thermal expansion: $\Delta\alpha/\Delta P = -1.52(2) \times 10^{-6} \text{ K}^{-1} \text{ GPa}^{-1}$. The errors reported here is estimated by equations of error propagation throughout the pressure correction procedures, where many fitted thermoelastic parameters are employed. The confidence interval and prediction errors for the fit are also presented in the diagram.

High P - T *in-situ* x-ray diffraction experiment provides the means for determining thermoelasticities 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. Thermodynamic properties are important for the understanding of phase relations for the enstatite-diopside-jadeite join in the upper mantle. Thermoelastic parameters of clinopyroxenes are essential for modeling of the seismic profile and the discontinuity at the top of transition zone related to pyroxene to garnet transition.

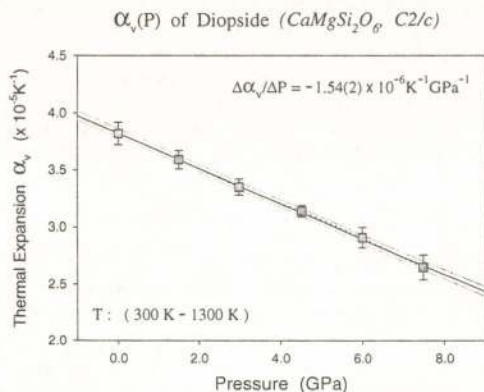


Fig 4. Thermal expansions of diopside $\text{CaMgSi}_2\text{O}_6$ plotted as a function of pressure. The slope of the fitted straight line represents pressure derivative of thermal expansion, $\Delta\alpha/\Delta P$. The width of the fitted line represents the confidence interval and the prediction error of the fit.

We have measured unit cell parameters for diopside and jadeite for pressure up to 8.2 GPa and temperature up to 1280 K [10]. These observations greatly extend our knowledge of pyroxene thermodynamics 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. 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: Diopside sample was provided by Dr. Gasparik. This work was supported by Institute of Geophysics and Planetary Physics and Laboratory-Directed Research and Development funding at Los Alamos. The SAM-85/NLSL project was supported by the NSF grant CHIIPR, EAR-8920239.

References

- [1] Y. Zhao and D. L. Anderson, *Phys. Earth Planet. Inter.*, **85**, 273-292, 1994.
- [2] H. M. Rietveld, *J. Appl. Cryst.*, **2**, 65-71, 1969.
- [3] A. C. Larson and R. B. Von Dreele, LAUR 86-748, Los Alamos, 1994.
- [4] D. L. Decker, *J. Appl. Phys.*, **42**, 3239-3244, 1971.
- [5] D. J. Weidner and SAM-85 team, *High Press. Res.*, **8**, 617-623, 1992.
- [6] Y. Zhao and SAM-85 team, *J. Geophys. Res.*, **99**, 2871-2885, 1994.
- [7] A. le Bail, H. Duroy, and J. L. Fourquet, *Mat. Res. Bull.*, **23**, 447-452, 1988.
- [8] Y. Zhao, R. B. Von Dreele, D. J. Weidner, *High Press. Res.*, **16**, 1-18, 1997.
- [9] F. Birch, *Phys. Review*, **71**, 809-824, 1947.
- [10] Y. Zhao, R. B. Von Dreele, T. J. Shankland, J. Zhang, D. J. Weidner, *Geophys. Res. Lett.*, **24**, 5-8, 1997.