	Experiment title: **$NaMgF_3$ Perovskite at High Pressures and Temperatures**	**Experiment number**:
Beamline: ID-30	**Date of experiment**: from: 14th May 2003 to: 15th May 2003	**Date of report**: 5th Nov 2003
Shifts: 12	**Local contact(s)**: Dr. W. A. Crichton	*Received at ESRF:*

Names and affiliations of applicants **(* indicates experimentalists):**

C. DAVID MARTIN[1]*, JOHN B. PARISE[1]*, WILSON A. CRICHTON[2]*

[1]Mineral Physics Institute & Department of Geosciences, State University of New York, Stony Brook, NY 11794-2100, USA

[2]European Synchrotron Radiation Facility, BP 220, F 38043 Grenoble, France

Report:

Introduction: The perovskite with general formula ABX_3, consists of corner-sharing BX_6 octahedra that surrounding A cations in 12-fold coordination. Interest in this unique structure stems, in part, from the central role of $MgSiO_3$ in Earth Science. This composition, in the perovskite structure, is believed to constitute the majority component in the lower mantle, and unexpected lateral variations in seismic velocities in this region (Woodhouse and Dziewonski, 1989) might result from changes in temperature. This explanation is rationalized if dG/dT (G = shear modulus) is 2-4 times larger than dK_T/dT (Yeganeh-Haeri and Weidner, 1989).

Measurements of the structure, properties and phase transitions in $MgSiO_3$ at the pressure and temperature conditions of the lower mantle are difficult and so the study of a suitable analogue compound at more moderate conditions of P and T can provide insight. $NaMgF_3$ is orthorhombic and isostructural and isoelectronic with $MgSiO_3$; It is proposed as an ideal analogue material (O'Keeffe and Bovin, 1979). Previously, $NaMgF_3$ was shown to undergo a phase transition from orthorhombic (Pbnm) directly to cubic (Pm-3m) at elevated pressure and temperature with energy-dispersive x-ray diffraction, while dK/dT and $d\alpha/dP$ were both found to be 0 (Zhao et al., 1994). A value of zero for both dK/dT and $d\alpha/dP$ implies that compression and heating each have separate and different effects on sample structure. Zhao et al. (1994) suggest that changes in temperature tilts MgF_6 octahedra, while changes in pressure compress Mg-F bonds. We are interested in using angle dispersive x-ray diffraction to examine the effect of simultaneous pressure and temperature on: thermal expansion and compressibility, rotation of MgF_6 octahedrons, compression of Mg-F bonds, and the slope of the orthorhombic / cubic phase transition.

Methods and Materials: The polycrystalline sample of $NaMgF_3$ was prepared in air using conventional solid-state methods. Samples were mixed with 25 mol% B_4C to insure proper grain averaging throughout the experiment. Data collection was performed in angle-dispersive mode using a MAR imaging plate. Simultaneous EOS of BN and Au was used to determine pressure and temperature, further details of the experimental setup can be found elsewhere (Crichton and Mezouar, 2002).

Results: A total of 331 angle dispersive x-ray diffraction patterns were collected during beamtime. Our analysis confirms that $NaMgF_3$ transforms from orthorhombic directly to cubic at all pressures and temperatures examined (up to 6 GPa and 1400°C). Also, we find a much steeper slope for the phase transition than was found previously 130 vs. 45 K/GPa (Zhao et al., 1994). This discrepancy may be a result of poor grain averaging in the Zhao (1994) study, as we find that without an inert secondary phase to buffer contact between grains, $NaMgF_3$ readily and quickly consolidates crystallites at high temperature. A preliminary second-order fit of the Birch-Murnaghan equation of state to data yields the following constants: $K_O = 59.4 \pm 1.1$ GPa, $\alpha_O = 9.23 \pm .58$ K^{-1}, and $dK/dT = -0.016 \pm .0039$ GPa•K^{-1}. The effect of pressure and temperature on atomic positions and bond lengths using Rietveld refinement is currently ongoing.

Conclusions: With the preliminary finding that compressibility of $NaMgF_3$ changes substantially with temperature, we are able to conclude (using $NaMgF_3$ as an analogue and assuming lateral temperature variations co-occur with large lateral $dlnV_S/dlnV_P$ values) that values of dG/dT for $MgSiO_3$ must be anomalously large relative to other lower mantle silicate and oxide phases to be ultimately responsible for lateral variations in seismic velocities. One must then examine the effect of perovskite phase transitions and/or regions of melt as a possible explanation.

Acknowledgments: This work acknowledges support from the DOE and NSF-EAR grants.

References:

Crichton, W.A., and Mezouar, M. (2002) Noninvasive pressure and temperature estimation in large-volume apparatus by equation-of-state cross-calibration. High Temperatures-High Pressures, 34(2), 235-242.

Okeeffe, M., and Bovin, J.O. (1979) Solid Electrolyte Behavior of $NaMgF_3$ - Geophysical Implications. Science, 206(4418), 599-600.

Woodhouse, J.H., and Dziewonski, A.M. (1989) Seismic Modeling of the Earths Large-Scale 3-Dimensional Structure. Philosophical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences, 328(1599), 291-&.

Yeganehhaeri, A., and Weidner, D.J. (1989) Elasticity of $MgSiO_3$ in the Perovskite Structure. Science, 243(4892), 787-789.

Zhao, Y.S., Weidner, D.J., Ko, J.D., Leinenweber, K., Liu, X., Li, B.S., Meng, Y., Pacalo, R.E.G., Vaughan, M.T., Wang, Y.B., and Yeganehhaeri, A. (1994) Perovskite At High P-T Conditions - an in-Situ Synchrotron X- Ray-Diffraction Study of $NaMgF_3$ Perovskite. Journal of Geophysical Research-Solid Earth, 99(B2), 2871-2885.