Structural investigation of pyrope garnet using temperature-dependent FTIR and ^{29}Si and ^{27}Al MAS NMR spectroscopy

Charles A. Geiger

Bayerisches Geoinstitut, Universität Bayreuth, Postfach 10 12 51, W-8580 Bayreuth, Germany
and Universität Kiel, Mineralogisch-Petrographisches Institut, Olshausenstraße 40, W-2300 Kiel 1, Germany

Lawrence Merwin, Angelika Sebald

Bayerisches Geoinstitut, Universität Bayreuth, Postfach 10 12 51, W-8580 Bayreuth, Germany

Abstract

Pyrope garnet, $Mg_3Al_2Si_3O_{12}$, has a relatively large third-law entropy that is thought to be strongly influenced by the structural environment and the motion of Mg in the dodecahedral site. Pyrope has been synthesized at two temperatures (1723 and 1273 K) and studied by powder FTIR spectroscopy between 310 and 100 K and by ^{27}Al and ^{29}Si MAS NMR spectroscopy. The FTIR spectra, measured on pyrope synthesized at a very high temperature, show little change upon cooling to 100 K. The ^{29}Si MAS NMR spectra for pyrope synthesized at 1723 and 1273 K show no differences in their chemical shifts or peak widths. MAS NMR spectra obtained from a natural nearly end-member pyrope from Dora Maira show line broadening resulting from a small amount of an almandine component in solid solution. These spectroscopic results are consistent with X-ray diffraction data that indicate that the large displacement parameters for Mg^{2+} in pyrope can be largely explained as a result of anisotropic dynamic disorder and not static subsite positional disorder, at least to 100 K (Armbruster et al., 1992).

Introduction

Pyrope garnet, $Mg_3Al_2Si_3O_{12}$, is not stable at low pressures and must therefore be synthesized at elevated pressures (Boyd and England, 1959). This is consistent with the occurrence of natural pyrope-rich garnet in high-pressure metamorphic rocks and in mantle peridotites and eclogites. In the pyrope structure the Mg cation shows measurable anisotropic dynamic disorder (Armbruster et al., 1992) and, because of the potential instability of Mg within the large dodecahedral site, the pyrope structure could conceivably undergo a phase transformation at low temperatures. Moreover, this strong vibrational amplitude of the Mg cation, which changes markedly with temperature, could have an important effect on pyrope's heat capacity, relative to the other aluminosilicate garnets.

The best way to investigate experimentally possible structural modifications and to understand the nature of atomic motions is to undertake temperature-dependent diffraction (Armbruster et al., 1992) and spectroscopic studies of well-characterized end-member pyrope at low-temperatures, where the thermal motion of all atoms is minimized and where site ordering of Mg could occur. Combining methods to probe the pyrope structure at different correlation lengths and time scales is necessary to understand both the local and unit-cell averaged symmetries and the dynamics within the structure. We report here low-temperature powder FTIR and MAS ^{29}Si and ^{27}Al NMR spectra to understand better the local structural relations. An earlier paper discusses the average long-range structural properties and previous crystallographic proposals concerning possible Mg dodecahedral subsite ordering in pyrope garnet (Armbruster et al., 1992).

The vibrational spectrum of synthetic pyrope has been measured previously at room temperature by infrared (IR) powder techniques (Cahay et al., 1981; Geiger et al., 1989; McMillan et al., 1989). The last group also reported Raman and ^{27}Al NMR spectra. High-pressure IR spectra to 50 kbar at 25, 100, and 250 °C of a natural pyrope almandine garnet were measured by Dietrich and Arndt (1982), as were the Raman spectra to 13.7 GPa of end-member pyrope by Mernagh and Liu (1990). Hofmeister and Chopelas (1991a) presented polarized single-crystal Raman and infrared reflection measurements on five natural nearly end-member garnets, including pyrope, and assigned internal and lattice mode vibrations to the spectra. To date, however, no low-temperature IR or ^{29}Si MAS NMR spectra have been measured. The ^{29}Si MAS NMR data for pyrope at room temperature have been given in abstract form (Geiger et al., 1990a).

Experimental

Polycrystalline pyrope was synthesized using both hydrothermal and dry techniques from a glass of pyrope composition at 3.0 GPa and 1273 and 1723 K, respectively, in a piston-cylinder device. For the high-temperature synthesis (sample R-63) approximately 200 mg of pyrope glass was loaded into a Pt capsule with a 5-mm diameter, which was welded shut after baking out the

TABLE 1. MAS ^{29}Si NMR parameters for synthetic pyrope

Sample	T (K)	$\delta_{^{29}Si}$ (ppm)	$\nu_{1/2}$ (Hz)	$\nu_{1/2}$ (ppm)
R-63	298	−71.9	22	0.36
R-63	255	−72.0	22	0.36
Py-101/102	298	−72.0	27	0.45
Py-101/102	265	−72.0	27	0.45
Py-101/102	255	−72.0	27	0.45

unsealed capsule at 150 °C for several hours. The capsule was placed into a ¾-in. talc-glass assembly, with a tapered graphite furnace, which minimized thermal gradients (estimated at less than 25 °C across the capsule), and held at 1723 K and 3.0 GPa for 5 h. The experiment was quenched to room temperature from 1723 K with the pressure maintained by pumping during cooling. Quench times were about 10 s to 1073 K and 20 s to 673 K.

The hydrothermal syntheses were carried out in two separate experiments (Py-101 and Py-102). Approximately 200 mg of pyrope glass together with 25 μL of distilled H_2O were placed in large Au capsules with 5.5-mm diameters and then cold sealed (Cemic et al., 1990). They were held at 1273 K and 3.0 GPa in ¾-in. salt-based assemblies for 20 h.

All high-resolution solid state NMR spectra were obtained using a Bruker MSL 300 NMR spectrometer, equipped with double-bearing probes for both 4-mm and 7-mm rotors. Chemical shifts are given with respect to external Me_4Si equal to 0 ppm (using solid Q_8M_8 as a secondary reference; Engelhardt and Michel, 1987) for ^{29}Si, and with respect to aqueous $AlCl_3$ solution equal to 0 ppm for ^{27}Al (uncorrected for second-order quadrupolar effects). The ^{29}Si spectra were obtained on a 7-mm probe, with 2-μs, 36° pulses, single pulse excitation, 30-s relaxation delay, and spinning speeds of 3 kHz. In some cases the amount of the sample was insufficient to fill the rotor. In order to avoid mixing the samples with other materials, the ^{29}Si MAS spectra were measured using an airtight Kel-F rotor insert, designed to fit exactly the inner dimensions of the ZrO_2 rotor (ca. 100 mg of sample) (Merwin et al., 1989). Between 160 and 2500 transients were accumulated. All ^{27}Al MAS NMR spectra were measured on a 4-mm probe with spinning speed 8 kHz, $\pi/12$ pulses (= 1 μs), and relaxation delays of 1 s were sufficiently long to prevent saturation. Between 100 and 460 transients were accumulated.

Powder infrared spectra were recorded at Cambridge University by B. Winkler on a Bruker IFS 113v FTIR spectrometer employing the conventional pellet technique. Spectra were measured at ten temperatures between 310 and 100 K. Matrix material for the far infrared measurements (650–100 cm^{-1}) was polyethylene and, for those values in the midinfrared (1500–650 cm^{-1}), KBr was used. A total of 500 scans were recorded for each spectrum with a resolution of 1 cm^{-1}. A closed-cycle refrigerator (Leybold-Hereaus) was used for cooling, with
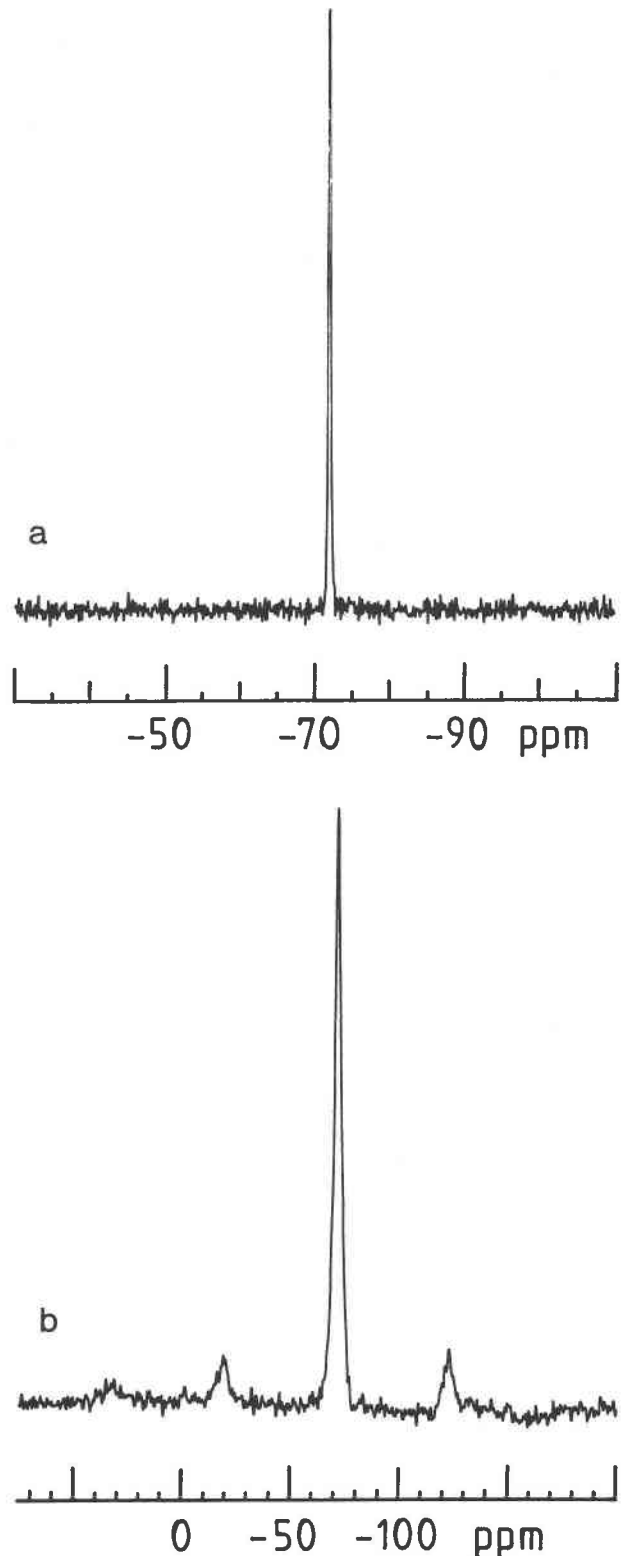

Fig. 1. (a) A ^{29}Si MAS NMR spectrum of pyrope synthesized at 1723 K and 3.0 GPa. The chemical shift is −72.0 ppm with a FWHM of 0.36 ppm. (b) A ^{29}Si MAS NMR spectrum of a natural nearly end-member pyrope from Dora Maira (Chopin, 1984). The chemical shift is −71.8 with a FWHM of 3.2 ppm.

Fig. 3. FTIR spectra of pyrope (R-63) from 650 to 100 cm⁻¹ measured at 310 (top), 291 (middle), and 100 K (bottom).
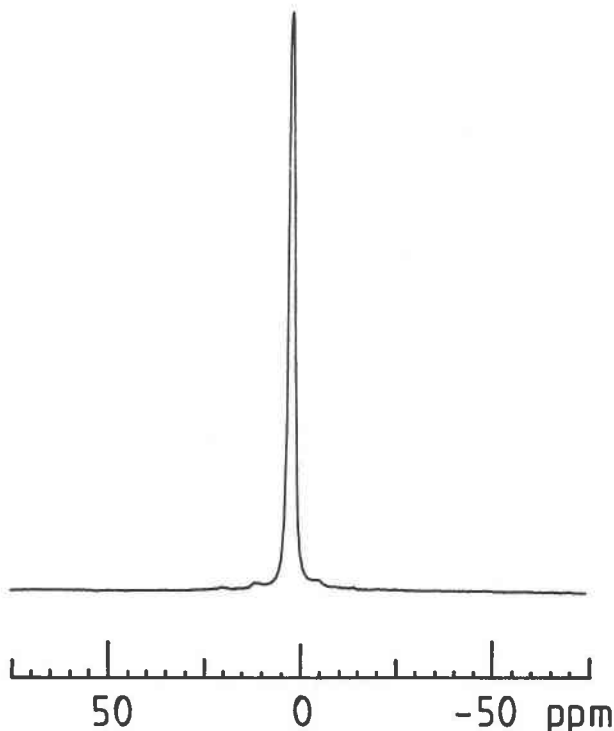

Fig. 2. A ^{27}Al MAS NMR spectrum of pyrope synthesized at 1273 K and 3.0 GPa. The spinning speed was 8 kHz.

the pellet inside a sample holder made from O-depleted Cu to provide good thermal stability.

RESULTS

The polycrystalline product materials (R-63, Py-101, and Py-102) were examined by optical microscopy and powder X-ray diffraction. The syntheses yielded greater than 99.5% pyrope. X-ray diffraction patterns showed a very small amount of quartz (<0.5%), based on the presence of the small 101 diffraction peak just noticeable above the background. The compositions of the pyrope samples were not determined with the electron microprobe, but deviations from stoichiometry are assumed slight, based upon the characterization of synthetic pyrope garnet described by Geiger et al. (1991).

The ^{29}Si MAS NMR spectrum of the pyrope synthesized hydrothermally at 1273 K shows a single sharp resonance with a chemical shift of −72.0 ppm and a full width at half maximum (FWHM) of 0.45 ppm. Only one Si resonance is present, indicating that only a single Si site is present in the local structure, as it is in the average long-range structure in pyrope of space group $Ia\bar{3}d$. The results of all the measurements are listed in Table 1. Figure 1a shows the ^{29}Si NMR spectrum taken from pyrope synthesized at 1723 K (R-63) and 30 GPa. It has a chemical shift of −71.9 ppm and FWHM of 0.36 ppm. Figure 1b shows the ^{29}Si spectrum measured from a natural nearly end-member pyrope from the Dora Maira Massif (Chopin, 1984). It has a chemical shift of −71.8 and a
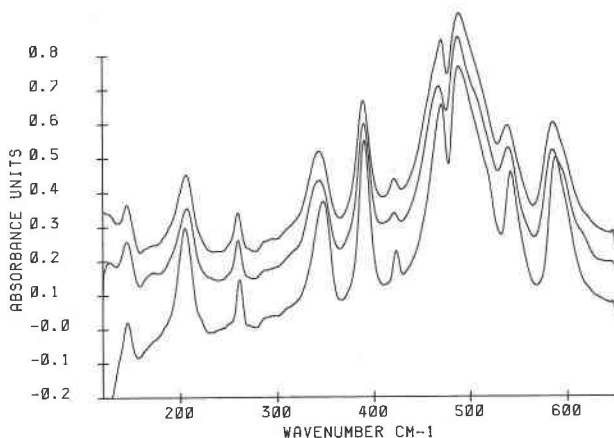
broad FWHM of 3.2 ppm. This broadening is a result of a small amount of paramagnetic Fe^{2+} (approximately 2.0 wt% FeO), and therefore, for quantitative structural comparisons, the NMR spectra of natural garnets are unsatisfactory. The ^{27}Al spectrum of the pyrope synthesized at 1273 K (Py-101, Py-102) was also measured, and it shows a single resonance with a chemical shift of 1.8 ppm and a FWHM of 1.8 ppm (Fig. 2). The ^{27}Al spectrum of the Dora Maira pyrope also displays a broadened resonance at 1.9 ppm. McMillan et al. (1989) reported a chemical shift of 2.8 ppm for synthetic pyrope. The ^{29}Si spectra recorded at 265 and 255 K show no change with respect to chemical shift and FWHM compared to the room temperature measurements (Table 1).

The powder IR spectra at three temperatures, 310, 291, and 100 K, on the pyrope synthesized at 1723 K (R-63), are shown in the energy region from 600 to 150 cm⁻¹ (Fig. 3). The room temperature spectrum is the same as previously published powder pyrope spectra (Cahay et al., 1981; Geiger et al., 1989; McMillan et al., 1989). There are also no major differences between the spectra at 310 and 100 K (Fig. 3). Most modes simply become sharper with decreasing temperature. Table 2 gives the peak positions of the bands at two temperatures.

DISCUSSION

Low-temperature adiabatic heat-capacity measurements undertaken on synthetic pyrope show that it has a large third-law entropy that cannot be estimated by simple oxide summation methods (Haselton and Westrum, 1980). Haselton and Westrum's experimentally measured third-law entropy value of 266.27 J/mol·K at 298 K was in good agreement with that calculated from high-temperature phase equilibrium data, and therefore they proposed that no Mg^{2+} dodecahedral site disorder exists in pyrope (Haselton and Westrum, 1980). The first model heat-capacity estimations (Kieffer, 1980), based on phonon density of state calculations, gave a third-law entropy for pyrope that was in reasonable agreement with the

TABLE 2. Far infrared peak positions of pyrope (R-64) at 100 and 310 K

Mode assignment*	At 100 K (cm^{-1})	FWHM	At 310 K (cm^{-1})	FWHM
ν_4	542	19	539	30
ν_2	488	48	487	54
T(Al)	471	34	467	43
T(Al)	423	14	421	41
R(SiO$_4$)	390	15	390	19
T(SiO$_4$)	348	23	344	34
T(M)	261	8	260	11
T(M)	205	16	207	23
T(SiO$_4$)	146	13	145	16

* Hofmeister and Chopelas (1991a).

calorimetrically measured value. However, Kieffer pointed out the discrepancy regarding the larger entropy for pyrope compared to that of grossular garnet, despite the lighter mass of the former. She proposed that the excess entropy in pyrope could be a result of strongly asymmetric vibrations of the Mg cation. Hofmeister and Chopelas (1991b) refined Kieffer's model calculations using their more precise and extensive optical vibration measurements (IR and Raman) made on single crystals. Their model C_P values are generally in good agreement with the experimental C_P values of Haselton and Westrum (1980), except between 50 and 150 K, where they are slightly lower. This difference, which produces an excess heat capacity in the calorimetrically measured pyrope, was attributed to possibly subsite disorder of the Mg cation in the pyrope, which was synthesized at temperatures of 1623–1673 K.

The ^{29}Si and ^{27}Al MAS NMR spectra are consistent with well-ordered pyrope with no measurable disorder, as no differences were observed in the chemical shifts and FWHM between the ^{29}Si MAS NMR spectra of pyrope synthesized at 1273 and 1723 K. Moreover, the narrow FWHM of 36 ppm for the Si peak of pyrope R-63 indicates that the pyrope is well ordered. The Si site in garnet is relatively sensitive to its surrounding environment because first neighbor dodecahedral cation and, in addition, second shell dodecahedral interactions are recorded for pyrope grossular garnets (Geiger et al., 1990b).

The powder FTIR results show no new additional bands, discontinuous shifts, peak splittings, or soft modes between 310 and 100 K, therefore giving no evidence for any temperature-dependent phase change. The IR measurements support the X-ray refinement results that demonstrate that the Mg^{2+} cation exhibits measurable dynamic anisotropic thermal disorder (Armbruster et al., 1992), but no measurable positional subsite Mg disorder to at least 100 K (Zemann and Zemann, 1961; Kleber et al., 1969; Cressey, 1981; Hofmeister and Chopelas, 1991b).

No change or splittings in the two vibrational bands located at approximately 260 and 210 cm^{-1}, which have been assigned to Mg dodecahedral translations (Hofmeister and Chopelas, 1991a), were observed. Therefore,

no symmetry changes in the dodecahedral site seem apparent. The IR spectra show no evidence for symmetry changes at low temperatures, which would probably be necessary if subsite ordering occurred in the symmetry fixed X site of 222 point symmetry. The ^{57}Fe Mössbauer spectra measured on the garnet almandine show an anisotropic recoil-free fraction of Fe^{2+} in the dodecahedral site resulting from a similar anisotropic motion (Geiger et al., 1992). These measurements made down to 15 K are consistent with thermal disorder within the dodecahedral site. The similarities between the pyrope and almandine structures support the view that no measurable static X-site disorder has yet been experimentally substantiated in aluminosilicate garnet.

The large thermal motion of the Mg cation can probably account for the relatively large third-law entropy of pyrope. Haselton and Westrum (1980) suggested that an increased vibrational amplitude of Mg in garnet of composition pyrope$_{60}$grossular$_{40}$ generates an excess heat capacity at low temperatures. The Ca cation in grossular shows smaller atomic displacement parameters at a given temperature than that of pyrope (Meagher, 1975), and this is consistent with its smaller third-law entropy (Haselton and Westrum, 1980). Navrotsky (1980) discussed some of the crystal chemical and petrological implications resulting from the large third-law entropies inherent in high-pressure phases, where small cations reside in sites of high coordination. Anomalous vibrations of small cations and anharmonic vibrations within the crystal are thought to be important in giving rise to large third-law entropies.

It is possible that model heat capacity calculations on pyrope and almandine garnets need to account or correct for either (1) dispersion relations across the Brillioun zone, (2) unobserved inactive or very weak modes, (3) Fe and Mg anharmonicity, or (4) incorrectly assigned vibrational modes, before quantitative heat capacities can truly be calculated. For example, Olijnyk et al. (1991) concluded that a broad low-energy band present at approximately 145 cm^{-1} in the pyrope Raman spectrum is a fundamental lattice mode and, therefore, should be considered in any density of state calculation. It may be related to a split-frequency vibration resulting from the strong asymmetric motion of the Mg cation, as proposed by Kieffer (1980). The ΔU values along the Mg-O4 bonds increase with increasing temperature, which produces a nonrigid body vibration (Armbruster et al., 1992) and may therefore give rise to broadened or slightly split peaks for those vibrations originating in the dodecahedral site. Very weak modes lying below 150 cm^{-1} should also be carefully searched for.

The effect of anharmonic contributions to the modeled heat capacities needs also to be considered before small heat-capacity differences, such as those that are expected to generate excess third-law entropies of mixing in silicate solid solutions, can be calculated. Empirical corrections for anharmonic vibrations, which become important at higher temperatures, have been made in silicate and ox-

ide structures (i.e., Gillet et al., 1990), and their effect on the calculated heat capacities of garnet should now be considered.

REFERENCES CITED

Armbruster, T., Geiger, C.A., and Lager, G.A. (1992) Single-crystal X-ray structure study of synthetic pyrope almandine garnets at 100 and 293 K. American Mineralogist, 77, 512–521.

Boyd, F.R., and England, J.L. (1959) Pyrope. Carnegie Institution of Washington Year Book, 1958–1959, 83–87.

Cahay, R., Tarte, P., and Fransolet, A.-M. (1981) Interpretation du spectre infrarouge de varietes isotopiques de pyropes synthetiques. Bulletin de Minéralogie, 104, 193–200.

Cemic, L., Geiger, C.A., Hoyer, W.W., Koch-Müller, M., and Langer, K. (1990) Piston-cylinder techniques: Pressure and temperature calibration of a pyrophyllite-based assembly by means of DTA measurements, a salt-based assembly, and a cold sealing sample encapsulation method. Neues Jahrbuch für Mineralogie Monatshefte, 49–64.

Chopin, C. (1984) Coesite and pure pyrope in high-grade blueschists of the western Alps: A first record and some consequences. Contributions to Mineralogy and Petrology, 86, 107–118.

Cressey, G. (1981) Entropies and enthalpies of aluminosilicate garnets. Contributions to Mineralogy and Petrology, 76, 413–419.

Dietrich, P., and Arndt, J. (1982) Effects of pressure and temperature on the physical behavior of mantle-relevant olivine, orthopyroxene and garnet. In W. Schreyer, Ed., High-pressure researches in geoscience, p. 307–319. Schweitzerbart'sche Verlagsbuchhandlung, Stuttgart.

Engelhardt, G., and Michel, D. (1987) High-resolution solid-state NMR of silicates and zeolites, 485 p. Wiley, New York.

Geiger, C.A., Winkler, B., and Langer, K. (1989) Infrared spectra of synthetic almandine-grossular and almandine-pyrope garnet solid solutions. Mineralogical Magazine, 53, 231–237.

Geiger, C.A., Merwin, L., and Sebald, A. (1990a) Ordering studies in grossular and pyrope garnets using ^{29}Si NMR and ^{57}Fe Mössbauer spectroscopy (abs.). Third International Symposium on Experimental Mineralogy, Petrology and Geochemistry, p. 11–12. Blackwell Scientific, Oxford, U.K.

——— (1990b) Pyrope-grossular garnets: Synthesis and ^{29}Si MAS NMR spectroscopy (abs.). American Geophysical Union Fall Meeting, San Francisco, 1666.

Geiger, C.A., Langer, K., Bell, D.R., Rossman, G.R., and Winkler, B. (1991) The hydroxide component in synthetic pyrope. American Mineralogist, 76, 49–59.

Geiger, C.A., Armbruster, T., Jiang, K., Langer, G.A., Lottermoser, W., and Amthauer, G. (1992) A combined temperature dependent ^{57}Fe Mössbauer and single crystal X-ray diffraction study of synthetic almandine: Evidence for the Gol'danskii-Karagin effect. Physics and Chemistry of Minerals, in press.

Gillet, Ph., Le Cleac'h, A., and Madon, M. (1990) High-temperature Raman spectroscopy of SiO_2 and GeO_2 polymorphs: Anharmonicity and thermodynamic properties at high-temperatures. Journal of Geophysical Research, 95, 21635–21655.

Haselton, H.T., and Westrum, E.F., Jr. (1980) Low-temperature heat capacities of synthetic pyrope, grossular, and pyrope$_{60}$grossular$_{40}$. Geochimica et Cosmochimica Acta, 44, 701–709.

Hofmeister, A.M., and Chopelas, A. (1991a) Vibrational spectroscopy of end-member silicate garnets. Physics and Chemistry of Minerals, 17, 503–526.

——— (1991b) Thermodynamic properties of pyrope and grossular from vibrational spectroscopy. American Mineralogist, 76, 880–891.

Kieffer, S.W. (1980) Thermodynamics and lattice vibrations of minerals: Application to chain and sheet silicates and orthosilicates. Reviews of Geophysics and Space Physics, 18, 862–886.

Kleber, W., Jost, K.H., and Ziemer, B. (1969) Zur Koordination des Magnesiums im Pyrop und Untersuchungen über dessen thermische Zersetzung. Kristall und Technik, 4, 423–429.

McMillan, P., Akaogi, M., Ohtani, E., Williams, Q., Nieman, R., and Sato, R. (1989) Cation disorder in garnets along the $Mg_3Al_2Si_3O_{12}$-$Mg_4Si_4O_{12}$ join: An infrared, Raman and NMR study. Physics and Chemistry of Minerals, 16, 428–435.

Meagher, E.P. (1975) The crystal structure of pyrope and grossularite at elevated temperatures. American Mineralogist, 60, 218–228.

Mernagh, T.P., and Liu, L. (1990) Pressure dependence of Raman spectra from the garnet end-members pyrope, grossularite and almandine. Journal of Raman Spectroscopy, 21, 305–309.

Merwin, L.H., Sebald, A., Espidel, J.E., and Harris, R.K. (1989) An air-tight, inexpensive, easy to use MAS rotor insert. Journal of Magnetic Resonance, 84, 367–371.

Navrotsky, A. (1980) Lower mantle phase transitions may generally have negative pressure-temperature slopes. Geophysical Research Letters, 7, 709–711.

Olijnyk, H., Geiger, C.A., Schneider, H., Wokaun, A., and Häfner, W. (1991) Effect of composition and pressure on the Raman spectra of almandine-pyrope garnets. Terra Abstracts, 3 (1), 68.

Zemann, A., and Zemann, J. (1961) Verfeinerung der Kristallstruktur von synthetischem Pyrop, $Mg_3Al_2(SiO_4)_3$. Acta Crystallographica, 14, 835–837.