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The symmetry of garnets on the pyrope ($Mg_3Al_2Si_3O_{12}$) - majorite ($MgSiO_3$) join

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Abstract. Garnets with compositions between majorite and pyrope, Mj_{38}, Mj_{48}, Mj_{75} and Mj_{79} were synthesized at high pressures and temperatures in a 2000-ton uniaxial split-sphere apparatus (USSA-2000) and investigated using high resolution synchrotron X-ray powder diffraction and transmission electron microscopy. The results from both techniques are consistent with the tetragonal field for these garnets extending to a majorite composition just below Mj_{75}. The cubic-tetragonal structural phase transition in garnet along the majorite - pyrope join is sensitive to both composition and temperature and is expected to result in anomalous behavior in elastic shear moduli. This phase transition may occur in the transition zone of the earth's mantle and will have important effects on the elastic and rheological properties of this region where these garnets are stable phases.

Introduction

Garnet rich in the Majorite component ($Mg_4Si_4O_{12}$) is an important mineral phase in the transition zone of the Earth's mantle at depths of 300-700 km (Ringwood, 1967; Liu, 1977; Akaogi and Akimoto, 1977; Ito and Takahashi, 1987; Kanzaki, 1987; Gasparik, 1989). At these pressures, the garnet component makes up about 40% by volume for peridotitic compositions and as much as 60% for basaltic or eclogitic compositions (e.g., Irifune and Ringwood, 1987; Weidner and Ito, 1987; Ita and Stixrude, 1992). As such, the physical properties of this phase and phases on the $Mg_4Si_4O_{12}$ (Majorite)- $Mg_3Al_2Si_3O_{12}$ (Pyrope) join are of consequence for this region of the Earth (Jeanloz, 1981; Yeganeh-Haeri et al., 1990; Bass and Kanzaki, 1990; Yagi et al., 1987, 1992; Rigden et al., 1994; Sinogeikin et al., 1996; Pacalo and Weidner, 1996).

The end members of the pyrope-majorite series have well established symmetries and crystal structures. Pyrope (Py) is cubic, $Ia\bar{3}d$(Armbruster et al., 1992). Majorite (Mj) synthesized at 18 GPa and 1800° C and recovered at ambient conditions is tetragonal, $I4_1/a$ with Mg and Si on two different octahedral positions (Angel et al., 1989; see also Matsubara et al., 1990; Pacalo and Weidner, 1996) These differences in crystal symmetry and structure may have significant effects on the elasticity and other physical properties (e.g., Hatch and Ghose, 1989; McMillan et al., 1989; Sinogeikin et al., 1996). In particular, the transformation from $Ia\bar{3}d$ to $I4_1/a$, being an improper ferroelastic transition, should result in a decrease in selected elastic moduli due to mode softening (Hatch and Ghose, 1989; see also discussion in Wang et al., 1993). Various compositional models imply a wide range of majorite content in garnets in the transition zone (roughly from 45 to 80%); the potential anomalous behavior in the shear moduli across the transition will have significant consequences for mineralogical models of this region of the earth's interior.

It is therefore important to establish the influence of pyrope solubility on the elasticity and crystal symmetry of compositions along the pyrope-majorite join. To this end, we have prepared in our laboratory a series of polycrystalline materials synthesized at high pressures and temperatures (following the phase diagram of Gasparik, 1992) and begun to determine their elastic properties and thermal equations of state (Rigden et al., 1994; Pacalo and Weidner, 1996; Wang et al., 1996). The purpose of this paper is to report our investigation of the crystal symmetry across this solid-solution series.

Experiment Methods

1. Sample Description

The materials examined were synthesized using the 2000-ton, uniaxial split-sphere high pressure apparatus (USSA-2000) in the High Pressure Laboratory at Stony Brook (Table 1). All of the samples, except #2450, were recovered by following a P-T path for annealing, cooling and depressurization which is designed to preserve the high pressure phases and to relax the intergrannular stresses in the polycrystalline aggregates (see for example Fig. 1 of Rigden et al., 1994 and also Gwanmesia et al., 1993). Sample #2450 was quenched from the peak temperature condition, and then decompressed at room temperature. Transmission electron microscopy (TEM) indicates a much finer grain size and much higher dislocation density in this sample, compared to the others. Preliminary X-ray powder diffraction indicated polycrystalline, single phase materials had been produced. A summary of the chemical analysis for each sample, determined using a CAMECA microprobe, is given in Table 1.

2. High Resolution Synchrotron X-ray Powder Diffraction

Four compositions, 38%, 48%, 75% and 79%Mj, were ground and placed in glass capillaries of diameters 0.5, 0.7, 0.3 and 0.7 mm, respectively. These correspond to run numbers 1559, 1839, 2450 and 1923 in Table 1. Data for the determination of unit cell constants for the first three samples were collected in high resolution mode (Cox et al., 1988; Cox, 1992) using a Si(111) monochromator-Ge(220) analyzer combination. This mode

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Table 1. Synthesis conditions and properties of pyrope (Py)-majorite (Mj) specimens as determined by electron microprobe and synchrotron X-ray powder diffraction studies

sample	composition	run conditions P(GPa)/T(°C)/t(hr)	unit cell dimensions a (Å)	 c (Å)	 V(Å3)	reference
	Py100		11.452	-	1501.9	(1)
1559	Py62Mj38	18.0/1200/1.25	11.468(1)	-	1508.2	(2)
1839	Py52Mj48	18.6/1600/1.00	11.4735(5)	-	1510.4	(2)
2450	Py25Mj75	16.5/1600/1.33	11.4783(3)	-	1512.3	(2)
1923	Py21Mj79	19.8/1700/1.00	11.494(1)	11.457(1)	1513.6	(2)
	Mj100		11.515	11.429	1515.4	(3)

*starting materials were homogenous glasses of approximately the same composition as the final run products. For majorite compositions 40, 50 and 80%, the glasses were prepared by S. Kesson and S. M. Rigden at the ANU, Canberra. For the composition Mj75, the glass was prepared by D. Neuville at IPG in Paris.

involves considerable time for collection of data, but gives superior resolution and peak-to-background discrimination. More complete data sets suitable for Rietveld refinement (Rietveld, 1969) were collected for samples 2450 and 1923 (Table 1). These data were collected using both the crystal analyzer configuration and a linear position sensitive detector (psd) (Cox, 1992; Zhao et al., 1993). In those cases where tetragonal symmetry is encountered in the samples, it is useful to use structural information and the Rietveld methodology in the assignment of miller index for overlapped reflections (Rietveld, 1969; LeBail, 1988; Parise et al., 1993).

Step scans through the region of the $(400)_{cubic}$ reflection for the four samples are shown in Fig. 1. Scans through the region of the $(800)_{cubic}$ reflection show similar features; there are clearly two peaks for sample 1923 (with intensity ratios 1:2) instead of the one expected for a cubic material. This indicates the Mj79 material possesses tetragonal symmetry. Materials of composition 40 and 58% majorite are clearly cubic (Fig. 1) while sample 2450 (Mj75) also appears cubic, albeit with considerable broadening of the (400) peak. Unit cell parameters were obtained for these materials are compiled with other measurements in Table 1 and Fig. 2.

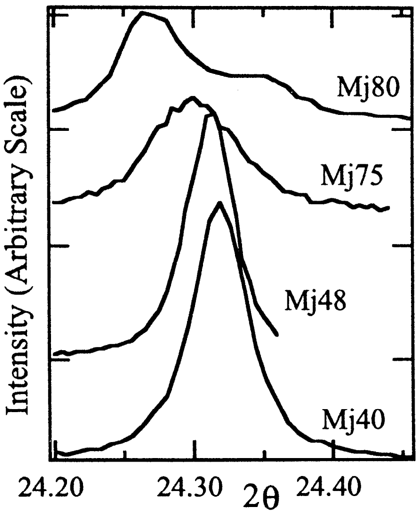

Fig.1. Step scan measurements in the region of the $(400)_{cubic}$ reflection for the compositions indicated (Table 1) using high resolution synchrotron X-ray powder diffraction with a monochromator/crystal-analyzer combination (Cox et al., 1988). The scans clearly indicate the cubic symmetry of compositions Mj38 and Mj48 and the tetragonal symmetry of the composition Mj79 since the $(400)_{cubic}$ peak of multiplicity 6 splits into the $(200)_{tetrag.}$ and $(002)_{tetrag.}$ with multiplicities 4 and 2 respectively. The symmetry of the garnet with composition Mj75 appears cubic but close inspection of weak intensities elsewhere in the pattern (Fig. 3) reveals it is tetragonal. The wavelength for these measurements (1.20810(4)Å) was determined from standard Si (a = 5.430825 Å).

In order to confirm the tetragonal symmetry of the Mj79 material, and to search for diffraction evidence of the symmetry of the Mj75 composition, the complete powder diffraction data sets were used in Rietveld refinements for these materials. The pattern of Mj75, collected using the psd, was also carefully scrutinized for evidence other than peak splitting, which would indicate symmetry lower than cubic. For the $Ia\bar{3}d$ symmetry of cubic garnets, the following classes of reflections are constrained thus: hh$l$; 2h + l = 4n and 0kl; k, l = 2n. The presence of the low angle reflections (222) and (031) (Fig. 3) which belong to the classes hh$l$ and 0kl but are not subject to the constraints for cubic symmetry, demonstrate that this garnet cannot be cubic but belongs most likely to the accepted tetragonal space group

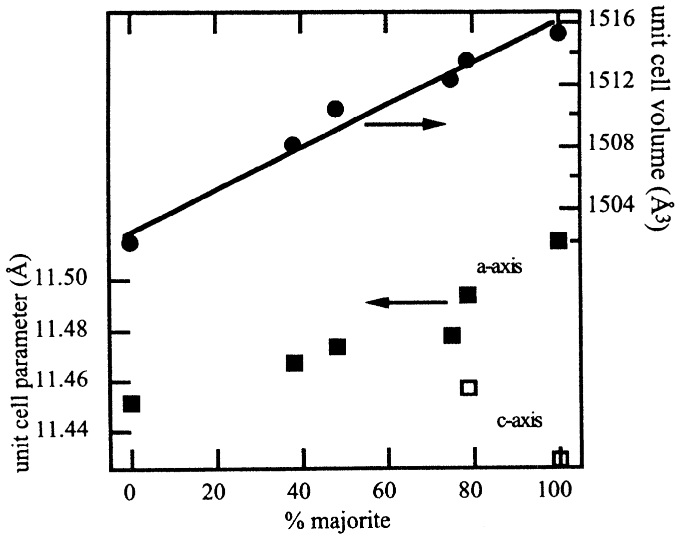

Fig. 2. Variation in cell volume (top) and unit cell parameters (bottom) as a function of composition for a series of materials along the pyrope ($Mg_3Al_2Si_3O_{12}$) - majorite ($Mg_4Si_4O_{12}$) garnet join. The values for the end member composition Py_{100} and Mj_{100} are taken from references cited in Table 1. The dashed line is a least squares fit to the data for the unit cell volume.

($I4_1/a$) for majorite (Angel et al. 1989). While these reflections are clearly visible above background in the diffraction pattern for Mj_{75}, they are an order of magnitude less intense than those for the Mj_{79} sample, when compared with the intense reflections common to both diffraction patterns (Fig. 3). This suggests that, although no splitting of the $(400)_{cubic}$ or $(800)_{cubic}$ is observed, the broadening evident in these reflections for the Mj_{75} sample (Fig. 1) is either the result of tetragonal symmetry or is a consequence of the sample consisting of a mixture of phases, at least one of which possesses tetragonal symmetry.

Results of the Rietveld refinement (Rietveld, 1969; Larson and Von Dreele, 1986) using the data from the Mj_{79} sample are consistent with the single crystal study (Angel *et al.*, 1989) including the space group assignment. However, the lack of scattering contrast between Mg^{2+}, Al^{3+} and Si^{4+}, which are isoelectronic, makes attempts to determine unique models for the distribution of cations over these sites fruitless using conventional refinement techniques. A Rietveld refinement was also carried out using the data collected for the Mj_{75} sample and a model based on published structural data (Angel, 1989). This resulted in tetragonal lattice parameters *a* and *c* converging to values equal to the cubic parameter shown in Table 1, within experimental error. Based on these data the change from cubic to tetragonal symmetry is placed at a majorite composition just below Mj_{75} (Figs. 1, 2 and 3). Further details of the structure refinements may be obtained from the authors.

3. Transmission Electron Microscopy (TEM)

In order to more completely characterize materials close to the cubic-tetragonal transition, specimens #2450 and 1923 with compositions Mj_{75} and Mj_{79} (Table 1) were examined using TEM. A modulated ("tweed") microstructure is clearly present throughout Mj_{79}, indicative of tetragonal symmetry (Wang et al., 1993) and consistent with the results of high resolution X-ray powder diffraction. The Mj_{75} sample was very fine grained (average grain size ~1 µm) and contained numerous dislocations, most likely due to the different P-T path during the synthesis of this sample; no definitive evidence of modulated microstructure could be obtained. Qualitative energy dispersive chemical analysis of several regions of the Mj_{75} sample suggested that it was homogeneous, on the scale of the order of 0.1 µm.

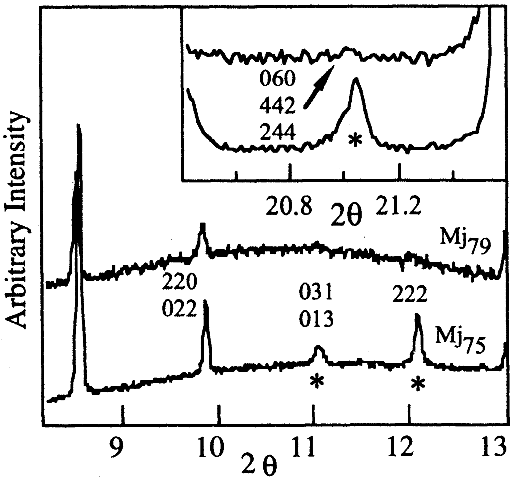

Fig. 3. Selected regions of the synchrotron X-ray powder diffraction patterns for samples 1923 (Mj_{79}, bottom curve) and 2450 (Mj_{75}, Table 1) collected with a psd at the X7A beamline, NSLS. The stars (*) indicates the positions of superlattice reflections which are expected to be absent for cubic garnets. Specifically, reflections belonging to the classes $0kl$; k, $l=2n$ (the 031 and 013) and the (hhl), $2h+l=4n$ (the (222) for example) are absent for cubic $Ia\bar{3}d$ symmetry. The inset also shows another of these peaks at a higher angle. For cubic $Ia\bar{3}d$ symmetry the (442) and (244) are symmetry equivalent (442) and belong to the class (hhl), $2h+l=4n$; the reflection (060), symmetry equivalent to the (006), belongs to this same class. Both classes are absent for cubic $Ia\bar{3}d$ symmetry and their presence in these patterns indicates tetragonal rather than cubic symmetry. The wavelength for these measurements (0.69827(9)Å) was determined from standard CeO_2 ($a = 5.4113$Å).

Discussion

The results of TEM and high resolution synchrotron X-ray powder diffraction are consistent with the tetragonal field for Py-Mj garnets extending from pure majorite to just below a composition of Mj_{75}. A plot of unit cell volume Vs. composition (Fig. 2) is monotonic and shows no obvious discontinuity close to the change over from cubic to tetragonal. The unit cell parameters on the other hand show a monotonic increase in *a* and a decrease in *c* as the majorite component increases (Fig. 2). The lattice parameters chosen for the $MgSiO_3$ end member in our analysis (Matsubara et al., 1990) are consistent with the trend in our data (Table 1, Fig. 1) and are considerably different from those obtained from the single crystal study (Angel, 1989). This either reflects the difficulties inherent in determining lattice parameters from twinned single crystals or may result from genuine differences in sample preparation. Interestingly, a recent single crystal study of a majorite sample essentially free of twinning, was carried out in our laboratories; the results of this study are consistent with the published powder diffractometry of Matsubara et al., 1990 (Pacalo and Weidner, 1996). The limited ability of X-rays to distinguish between models of the cation ordering in the tetragonal Mj-Py-garnets, necessitates the fall-back to crystal chemical arguments (e.g., Angel et al., 1989). Comparisons with other refined garnets of this type (Angel, 1989; Pacalo and Weidner, 1996) along with diffraction evidence that tetragonal symmetry persists to Mj_{75}, suggests some cation ordering also persists to about Mj_{75}; compositions richer in pyrope have no ordering on the octahedral sites, on the length scales probed by the X-ray and electron diffraction techniques employed in our investigations.

In their TEM study, Wang et al. (1993) concluded that a cubic-tetragonal phase transition occurs in the end member majorite near a temperature of 2350 °C. Combining their earlier observations with our new data, the cubic to tetragonal phase transitions in majorite-rich garnets depend on both temperature and majorite content. Various compositional models of the mantle will result in garnets with majorite contents ranging from ~ 50 mol% to 80%, a range encompassing the changeover from cubic to tetragonal symmetry.

This transformation from cubic, $Ia\bar{3}d$ to tetragonal, $I4_1/a$, is classified as an improper ferroelastic type transition (Hatch and Ghose, 1989). Such a transition should result in decreases in certain elastic moduli. Sinogeikin et al. (1996) have suggested that both the bulk and shear moduli decrease discontinuously near compositions of Mj_{80}, although an alternative model with a continuous decrease in moduli from pyrope to majorite (similar to that proposed by Pacalo and Weidner, 1996) cannot be excluded. Wang et al. (1996) report that the $Py_{62}Mj_{38}$ garnet exhibits normal thermoelastic behavior in a PVT experiment using in situ X-ray diffraction in a cubic multi-anvil apparatus (SAM 85), whereas the data for the $Py_{21}Mj_{79}$ garnet are anomalous and the microtwin domains in the specimen coarsen following cycling to 800°C at high pressures. In addition, Ando et al. (1996) have shown that the rheological properties of garnets along the pyrope-majorite join are strongly dependent on composition. Therefore, we conclude that the structural changes documented in this study have important consequences for both the elastic and rheological properties of these majoritic garnets in the transition zone of the Earth's mantle.

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