LETTER

Microscopic strain in synthetic pyrope-grossular solid solutions determined by synchrotron X-ray powder diffraction at 5 K: The relationship to enthalpy of mixing behavior

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ABSTRACT

A series of synthetic pyrope-grossular garnets ($Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$) were investigated by powder X-ray synchrotron radiation at 5 K to determine their microscopic structural strain, which may be responsible for the observed excess enthalpy of mixing for this binary. This substitutional solid solution provides an excellent system for investigating microscopic-macroscopic relationships and the physical nature behind non-ideal thermodynamic mixing behavior in silicates, because of the measurable nonidealities shown by its enthalpy and volume of mixing. An analysis of the X-ray refection profiles, based on theoretical considerations of X-ray line broadening, permits for the first time a direct experimental determination of crystallite size and the root-mean-square structural strain for a mineral solid solution. The measured microscopic strain shows positive and asymmetric deviations from linearity across the join with the largest excess in pyrope-rich compositions. There is a good correlation between the structural strain and the macroscopic enthalpy of mixing behavior for pyrope-grossular garnets as measured by calorimetry.

INTRODUCTION

There is much interest in the mineral sciences in understanding from a microscopic perspective the physical properties of Earth materials. One wants to understand in the case of minerals, for example, how microscopic properties control macroscopic properties such as the thermodynamic functions. Such study is especially challenging when considering substitutional solid solutions, because they are characterized by local chemical and structural heterogeneity. In this regard, it should be noted that most thermodynamic mixing models are phenomenological constructs (e.g., Guggenheim 1952; Ganguly 2001) that have little direct connection to local-scale crystal-structure properties. Lattice or structural strain arising from local structural heterogeneities in substitutional solid solutions is thought to produce elastic energies that strongly affect the macroscopic enthalpy and volume of mixing behavior (e.g., Christian 1975; Greenwood 1979; Ferreira et al. 1988; Geiger 2001), but experimental measurements that directly demonstrate this are virtually nonexistent.

The aluminum silicate garnets, $E_3Al_2Si_3O_{12}$, with E = Fe^{2+}, Mn^{2+}, Mg, and Ca, are rock-forming substitutional solid solutions important in various geochemical, petrological, and geophysical processes. Therefore, they have been the object of much crystal-chemical, structural, and thermodynamic study (for reviews see Geiger 1999, 2004). The aluminosilicate garnet structure has the space group $Ia\overline{3}d$, where the cations are located at special crystallographic positions and the oxygen atoms at a general position. The divalent E-cations occupy the 24c position of 222 point symmetry, the trivalent Al cations the 16a position of $\overline{3}$ symmetry, and the Si cation the 24d position with $\overline{4}$ point symmetry. The structure contains SiO_4 tetrahedra and AlO_6 octahedra that are connected through corners, thus building a three-dimensional quasi-framework. There exist small triangular-dodecahedral cavities in which the divalent E-cations are located, and it is here that mixing takes place. The pyrope-grossular ($Mg_3Al_2Si_3O_{12}$–$Ca_3Al_2Si_3O_{12}$) binary provides an excellent solid-solution system for the study of non-ideal thermodynamic behavior, because it shows marked positive deviations in its enthalpy (Newton et al. 1977), volume (Ganguly et al. 1993; Bosenick and Geiger 1997; Bosenick et al. 2001), and low-temperature heat capacity (Haselton and Westrum 1980) of mixing. The enthalpic non-ideality, as well as the volume non-ideality (Geiger 2000), is thought to result largely from elastic structural strain caused by the mixing of different sized Ca and Mg atoms at the E-site.

This proposal is supported by various crystal-chemical based calculations of elastic strain energies (Greenwood 1979; Ganguly et al. 1993), static lattice energy simulations using empirical pair potentials (Bosenick et al. 2000, 2001), lattice dynamic calculations of rigid unit modes (Hammonds et al. 1998), and through determinations of peak broadening of IR-active modes in the spectra of solid solutions (Boffa Ballaran et al. 1999). However, both the crystal-chemical models and the computational results have underlying weaknesses because of various assumptions that are built into them, and a quantitative physical basis for interpreting phonon line broadening for solid solutions has not yet been worked out. Thus, there is, even today after years of study, a notable lack of experimental results that bear on the question of how microscopic elastic strain affects the macroscopic thermodynamic mixing properties of silicate and oxide solid solutions (for a review see Geiger 2001).

EXPERIMENTAL METHODS

Data collection

The two end-members pyrope, $Mg_3Al_2Si_3O_{12}$, and grossular, $Ca_3Al_2Si_3O_{12}$, and seven intermediate garnet compositions were chosen for study. The garnets

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were previously synthesized under high pressure and temperature conditions and were carefully characterized with several experimental methods (Bosenick et al. 1995; Bosenick and Geiger 1997; Kolesov and Geiger 1998; Boffa Ballaran et al. 1999). Their compositions were determined by electron microprobe analysis (Bosenick et al. 1995) and they showed good compositional homogeneity and garnet stoichiometry.

The X-ray measurements were made at the European Synchrotron Radiation Facility (ESRF) at the powder diffraction beamline BM16, where the bending magnet beam-line optics encompasses a double-crystal Si(311) monochromator and vertically focusing optics. Low temperature measurements at 5 K were performed by means of a close-cycle liquid helium cryostat. A wavelength of 0.700127(2) Å was selected for the measurements and calibrated against elemental silicon (NBS 640b, having $a = 5.430954$ Å at 26 °C). The sample, included within a boron glass capillary (diameter 0.6 mm), was mounted on the ϕ axis of a two-circle diffractometer and axially rotated during the data collection in Debye-Scherrer geometry. Diffraction patterns were collected using the standard 9-channel detector available from 10 to 48° 2θ, with a step size of the rebinned histograms of 0.01° 2θ.

Theoretical background and evaluation of microstrain

The average internal microstrain in crystalline materials can be determined through X-ray reflection line broadening measurements using powder diffraction experiments (Wilson 1968; Balzar and Ledbetter 1993; Van Berkum et al. 1996). The theory was proposed years ago by Scherrer (1918) and successive developments (Stokes and Wilson 1944; de Keijser et al. 1983; Langford et al. 2000), mainly related to investigations of cold-metal working, showed that the shape of an X-ray diffraction line can be described by the convolution of instrumental aberration effects, $g(x)$, with the microstructure of the sample, $f(x)$:

$$h(x) = g(x)*f(x) \tag{1}$$

The profiles of Bragg diffraction peaks from real crystals reflect three physical effects, all of which are related to deviations from perfect crystal behavior. They are: (1) the size of the coherently diffracting crystal domains, commonly referred to as the crystallite size, (2) structural heterogeneity that is related to the presence of defects and vacancies and chemical inhomogeneity, all of which produce internal elastic strain, and (3) the vibrational properties of the atoms. The vibrational contribution, which is mostly accounted for by thermal motion (Artioli 2003), can be greatly minimized by making measurements at low temperatures. To evaluate the lattice strain, it is therefore necessary to deconvolve the instrument contribution from the experimental diffraction pattern, and then to separate the crystallite size and the strain components. The seminal works of Warren and Averbach (1952) demonstrated the possibility of separating the size and strain broadening components by their different dependence on the order of the reflection. Stokes (1948) later applied the Fourier deconvolution method to the troublesome problem of separating sample effects from instrumental contributions.

Stokes and Wilson (1944) defined the strain maximum (see Balzar 1999 for a review) as:

$$e = \frac{\Delta d}{d} = \frac{\beta_D(2\theta)}{4\tan\theta} = \frac{\beta_D}{2s} \tag{2}$$

where Δd represents the spread of d-values around the ideal value d, and β_D is the integral breadth of the peak in units of s ($s = 2\sin\theta/\lambda$, measured in Å^{-1}). The root mean square strain (e_{RMS}, hereafter referred to as RMS strain) is defined assuming a Gaussian distribution (Balzar 1999) as:

$$e_{RMS} = \left(\frac{2}{\pi}\right)^{1/2}\frac{\Delta d}{d} = \frac{\beta_D(2\theta)}{2s} \tag{3}$$

In other words, variations in the interplanar spacings, d, arising from local structural distortions, generate elastic strain. Reflection line broadening resulting from the solid-solution process in crystals is a small effect, however, and it can be obscured by larger instrumental contributions to the measured profile. Thus, quantitative X-ray studies on substitutional solid solutions are nonexistent due to the technical limitations imposed by most conventional diffractometers. The problem relating to aberration effects has now been lifted, though, with the construction of third-generation synchrotrons, because they provide the necessary instrumental resolution to enable sample-related broadening to be easily measured and quantified [the standard used herein to estimate the instrumental broadening is NAC ($Na_2Ca_3Al_2F_{14}$); Courbion and Ferey 1988]. In this study, data analysis was performed with the program MAUD (Material Analysis Using Diffraction; Ferrari and Lutterotti 1994) that allows for a simultaneous full-profile Rietveld structure refinement (Young 1993) and an analysis of the sample microstructure in terms of separate size and strain contributions. The program uses a convolutive method for the separation of the instrumental contribution from the total line broadening. An isotropic model for the strain is assumed, as we are working with a cubic lattice. Using this software, crystallite size and strain for the nine pyrope-grossular garnets were determined.

RESULTS AND DISCUSSION

Variations in reflection profiles between the two end-members pyrope and grossular and, as an example, an intermediate solid solution of composition Py60Gr40 are shown in Figure 1. The latter shows measurable peak broadening relative to the end-members. The calculated crystallite size and microstrain values along the pyrope-grossular join are shown in Figure 2. The mean crystallite size is markedly larger for grossular and pyrope than for most intermediate solid-solution compositions, reflecting the larger coherence of their diffracting domains. Conversely, the RMS strain is smallest for end-member grossular and pyrope. The intermediate solid solutions show smaller crystallite sizes and larger strain values that vary as a function of composition. This result is consistent with the observation that solid-solution garnets in synthesis experiments are fine-grained compared to the end members. The maximum strain values are observed for compositions between $X_{Ca} = 0.25$ and 0.40, while the lowest are found for end-members pyrope and grossular. The excess RMS strain values for each composition can be obtained by subtracting the value obtained from a linear interpolation of the end-member values (Fig. 3). The excess RMS strain can be described, by analogy with other excess thermodynamic properties, along the compositional join using a two-parameter mixing model of the type commonly used for fitting calorimetric enthalpy of mixing data:

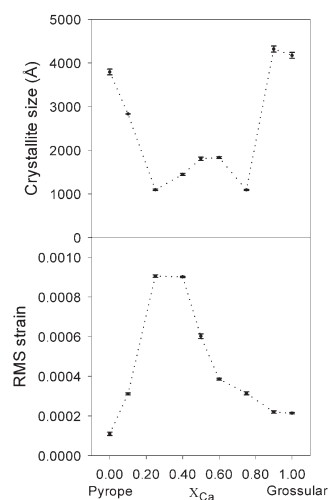$$\Delta strain^{ex} = W_{Mg-Ca}^{strain}(1 - x_{Ca})x_{Ca}^2 + W_{Ca-Mg}^{strain}(1 - x_{Ca})^2 x_{Ca} \tag{4}$$

where the W-terms can be considered as the elastic-strain-related interaction parameters and x_{Ca} the mole fraction of grossular in the garnet. The resulting best-fit values are $W_{Mg\text{-}Ca}^{strain} = -1.0(6)\cdot10^{-3}$ and
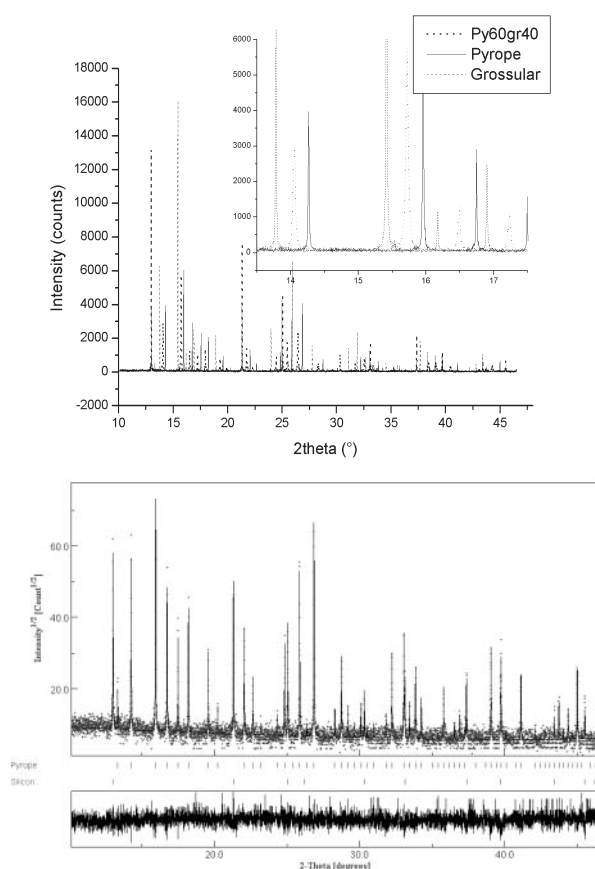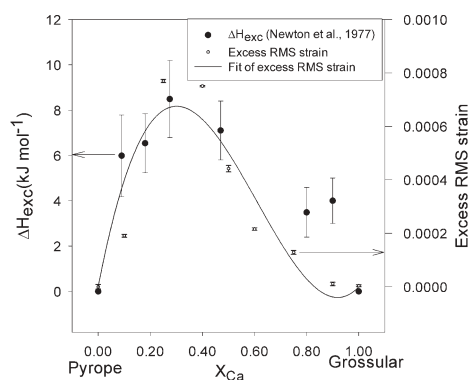
FIGURE 1. (**a**) Example of the variations in peak shapes for end-member pyrope (solid line), grossular (dashed line) and an intermediate composition (py60gr40 = dotted line); (**b**) example of the model fit for pyrope showing experimental data, the calculated spectrum, and the difference between the experimental and calculated intensities.

FIGURE 2. Crystallite size (top) and RMS strain (bottom) for pyrope-grossular solid solutions as a function of the mole fraction of Ca in garnet. The error bars represent 2σ variations in the determinations. The dotted lines are given to guide the eye.

FIGURE 3. Experimental values of the excess enthalpies of mixing (open squares from Newton et al., 1977) and the excess RMS strain (black circles). The error bars represent 2σ variations in the determinations. The solid line is a two parameter asymmetric fit (Eq. 4) to the excess RMS strain data.

$W_{Ca\text{-}Mg}^{strain} = 5.0(7)\cdot10^{-3}$. The solid line in Figure 3 shows the model fit to the X-ray data. This figure also shows the excess enthalpies of mixing determined by high-temperature solution calorimetry for the pyrope-grossular solid solution and the resulting two-parameter fit giving enthalpic (i.e., H) interaction parameters of $W_{Mg\text{-}Ca}^{H} = 16.4(9)$ kJ/mol and $W_{Ca\text{-}Mg}^{H} = 50.7(7)$ kJ/mol (Newton et al. 1977). The enthalpic deviations from ideality are positive, which is almost always the case for silicates and oxides (Geiger 2001), and are also asymmetric.

There is a good correlation between the X-ray determined excess RMS strain and the enthalpy of mixing behavior and this is a simple, yet important observation. It can be concluded that the asymmetric positive excess enthalpies in pyrope-grossular garnets are largely a result of microscopic elastic strain energy variations. They originate from local structural heterogeneities resulting from the mixing of different sized Mg (0.89 Å) and Ca (1.12 Å) atoms at the E-site. Strain is asymmetric as a function of composition and greater in pyrope-rich compositions, because it should be easier to incorporate the smaller Mg cation in a grossular-rich host than the larger Ca cation in a pyrope-rich host. It should be noted that strain for the solid-solution composition Py10Gr90 is similar to that for end-member grossular, which might indicate a plateau-type effect that is related to the size of

local strain fields around the substituting cations and their interactions with one another (Carpenter and Boffa Ballaran 2001). The garnet structure does not contain low-energy rigid modes related to simple SiO_4 or AlO_6 polyhedral rotation following the substitution of various E-cations. Thus, cation mixing must result in distortion of the strongly bonded tetrahedra and octahedra on a local scale (Hammonds et al. 1998) and this produces significant elastic energies. In contrast to our results, elastic strain energies derived from crystal-chemical models (Ganguly et al. 1993) predict nearly symmetric positive excess behavior about the 50:50 composition. Static lattice energy simulations (Bosenick et al. 2000, 2001) also give a nearly symmetric enthalpy of mixing behavior, whereas estimates based on IR line broadening predict a slight asymmetry toward grossular-rich compositions (Boffa Ballaran et al. 1999).

The diffraction experiment probes RMS strain over experi-

mental length scales comparable to those of the crystal domains (10^3 Å), whereas vibrational spectroscopy has shorter length scales. The two methods can be viewed as providing complementary information on structural heterogeneity and the nature of strain fields in substitutional solid solutions. X-ray measurements have the distinct advantage over vibrational spectroscopy in that the theory related to line broadening is better understood and strain can be calculated directly from X-ray powder patterns. Of course, for a more quantitative understanding of the macroscopic thermodynamic properties of solid solutions other energetic contributions such as electronic and magnetic effects must be considered in some cases.

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