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# Thermodynamics of (Fe$^{2+}$,Mn$^{2+}$,Mg,Ca)$_3$-Al$_2$Si$_3$O$_{12}$ garnet: a review and analysis*

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## Summary

The thermodynamic properties of garnets in the system (Fe$^{2+}$,Mn$^{2+}$,Mg,Ca)$_3$Al$_2$Si$_3$O$_{12}$ are reviewed. The thermodynamic properties of the three end-member garnets pyrope, almandine and grossular, including their volume, enthalpy of formation, entropy, compressibility and thermal expansion have been well determined. For spessartine enthalpy of formation and heat capacity at low temperatures are needed. Pyrope's unusual behavior in some of its properties is probably related to the presence of the small, light Mg cation, which has a large anisotropic thermal vibration. The thermodynamic mixing properties of the six binaries are also discussed. Good volume of mixing data exist now for all of the binaries, but much work is still required to determine the enthalpies and third-law vibrational entropies of mixing. It is shown that the magnitude of the positive deviations in the volumes of mixing is related to the volume difference between the two end-member components. It is probable that excess entropies, if present, originate at low temperatures below 200 K. Recent $^{29}$Si NMR experiments have demonstrated the presence of short-range ordering (SRO) of Ca and Mg in pyrope-grossular solid solutions. Short-range order will have to be considered in new models describing the entropies of mixing. Its possible presence in all garnet solid solutions needs to be examined. The mixing properties of pyrope-grossular garnets, which are the best known for any garnet binary, can, in part, be described by the Quasi-Chemical approximation, which gives insight into the microscopic interactions which determine the macroscopic thermodynamic mixing properties. Microscopic properties are best investigated by spectroscopic and computational approaches. Hard mode IR measurements on binary solid solutions show that the range of local microscopic structural distortion is reflected in the macroscopic volumes of mixing. The nature of

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strain fields and site relaxation needs to be studied in order to obtain a better understanding of the solid-solution process and energetics in garnet. Critical areas for future experimentation are also addressed.

## Zusammenfassung

*Eine kritische Zusammenstellung und Analyse der thermodynamischen Daten der $(Fe^{2+}, Mn^{2+}, Mg, Ca)_3 Al_2 Si_3 O_{12}$ Granate*

In dieser Studie werden die thermodynamischen Eigenschaften der Granate im System $(Fe^{2+}, Mn^{2+}, Mg, Ca)_3 Al_2 Si_3 O_{12}$ kritisch zusammengestellt. Die thermodynamischen Eigenschaften der drei Endglied-Granate Pyrop, Almandin und Grossular, einschließlich ihrer Volumina, Bildungswärmen, Entropien, Kompressibilitäten und thermischen Ausdehnungen wurden bereits hinreichend gut bestimmt. Dagegen müssen die Bildungswärme und Tieftemperatur-Wärmekapazität von Spessartin noch gemessen werden. Die Eigenschaften des Pyrops sind wahrscheinlich mit den großen anisotropen Schwingungen des kleinen, leichten Mg-Kations verbunden. Die thermodynamischen Mischungseigenschaften der sechs binären Mischkristallreihen werden ebenfalls diskutiert. Während die Mischungs-Volumendaten der binären Mischreihen gut bekannt sind, müssen ihre Mischungs-Enthalpien und Standard-Mischungsentropien noch ermittelt werden. Es wurde gezeigt, daß die Größe der positiven Exzeß-Volumina mit dem Volumen-Unterschied der zwei Endglied-Komponenten der jeweiligen Mischreihe verknüpft ist. Es ist wahrscheinlich, daß Exzeß-Entropien, wenn vorhanden, erst bei Tieftemperaturen unter 200 K auftreten. Neue $^{29}$Si NMR-Experimente belegen, daß in Pyrop-Grossular-Mischkristallen Nahordnung von Mg und Ca vorliegt. Der Effekt der Nahordnung muß in künftigen thermodynamischen Modellen berücksichtigt werden. Hieraus ergibt sich die Notwendigkeit, alle Granat-Mischreihen auf mögliche Nahordnung hin zu untersuchen. Die Mischungseigenschaften der Pyrop-Grossular-Mischreihe, die von sämtlichen Granat-Mischreihen am besten bestimmt wurden, können teilweise mit dem Quasi-Chemical-Model beschrieben werden. Dieses Modell ermöglicht die Beschreibung der mikroskopischen Wechselwirkungen, die die makroskopischen thermodynamischen Eigenschaften bestimmen. Mikroskopische Eigenschaften werden am besten mit spektroskopischen Messungen und theoretischen Berechnungen untersucht. Hard-mode IR-Spektroskopie-Messungen an binären Mischreihen zeigen, daß die lokalen mikroskopischen strukturellen Verzerrungen in den makroskopischen Mischungs-Volumina widergespiegelt werden. Die Art der Spannungsfelder und Platz-Relaxationen muß detaillierter untersucht werden, um ein besseres Verständnis des Mischkristall-Bildungsprozsses und der Energetik der Granate zu erreichen. Darüber hinaus werden wichtige künftige Forschungsgebiete diskutiert.

## Introduction

Garnet is one of the important silicate mineral groups found in Earth. It is a common phase in many crustal metamorphic mineral assemblages and in the upper mantle in garnet peridotites and eclogites. The aluminosilicate garnets, which can be described by the four component system $(Fe^{2+}, Mn^{2+}, Mg, Ca)_3 Al_2 Si_3 O_{12}$, are important for crustal metamorphic rocks and have, therefore, received much thermodynamic and phase equilibrium study over the years. There have been many attempts to describe the thermodynamic mixing properties of solid solutions within this system and a number of different models have been proposed. Unfortunately,

$$Mg_3Al_2Si_3O_{12}$$
Pyrope

Spessartine
$Mn_3Al_2Si_3O_{12}$

Almandine
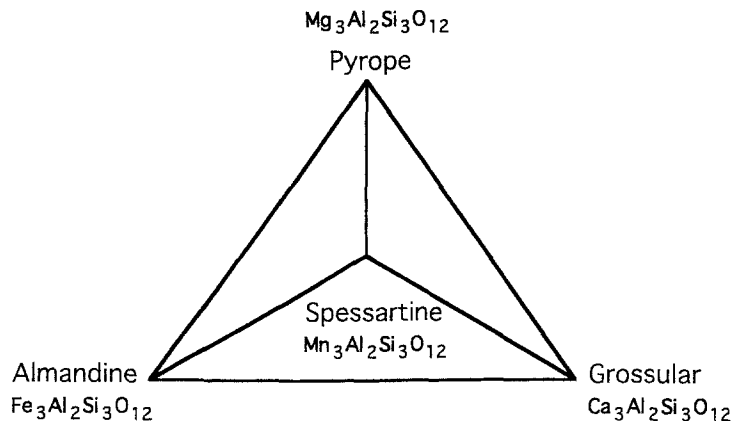$Fe_3Al_2Si_3O_{12}$

Grossular
$Ca_3Al_2Si_3O_{12}$

Fig. 1. Four component aluminosilicate garnet system almandine-pyrope-grossular-spessartine

the agreement among them is fair to poor. It is important at this stage to review and analyze the experimentally measured thermodynamic properties of the aluminosilicate garnets from the simplest level. It must be determined, first, what data are still needed and, second, which data are good and which not. It is essential to establish which results are sound and can be used for thermodynamic data bases and activity-composition models. Such a review can also point to further experiments which are required to improve and extend the existing data and to open up new avenues of research.

This review examines the thermodynamic properties of the four end-member garnets, almandine, pyrope, spessartine, and grossular and the six binary solid solutions within the $(Fe^{2+}, Mn^{2+}, Mg, Ca)_3Al_2Si_3O_{12}$ system (Fig. 1). The ternary and quaternary mixing properties will not be considered, because this author is of the opinion that there are too little results to make any definite statements. The thermodynamic data that are considered are taken mostly from calorimetric and X-ray measurements and to a lesser extent from P-T phase equilibrium experiments. The former type are direct measurements giving data which are not model dependent. They are given emphasis herein. In addition, the structural state and crystal-chemical properties, which bear upon the thermodynamic properties of garnet, will also be considered. In the past little attention has been given to the relationship(s) between structure and stability and microscopic structural and macroscopic thermodynamic properties. The time is now at hand where a complete integrated approach must be considered.

## Thermodynamic properties of the end-member garnets

The thermodynamic properties of the four end-member aluminosilicate garnets pyrope, grossular, almandine and spessartine have been determined well, with but a few gaps of knowledge. The equation which describes the Gibbs free energy, G, of a pure phase at P and T is given by:

$$G_{P,T} = H^0_{298\,K} - TS^0_{298\,K} + \int_{298\,K}^{T} C_P dT - T\int_{298\,K}^{T} (C_P/T)dT + \int_{1}^{P} V_{P,T}dP \quad (1)$$

where $H^0_{298\,K}$ is the standard enthalpy, $S^0_{298\,K}$ the standard entropy, $C_p$ the heat capacity, and V the volume. The standard state is defined as the pure substance at $P = 1$ bar and, T, the temperature of interest. The volume is the easiest property to determine experimentally.

## Volume

There have been a large number of determinations of the unit-cell constant, $a_0$, of the four end-member garnets over the past 40 years. There exists uncertainty regarding their correct values. Complications can arise because of the presence of additional components $(OH^-, Fe^{3+}, Mn^{3+})$ (*Geiger* et al., 1988; *Geiger* and *Feenstra*, 1997). For example, it may not be possible to synthesize stoichiometric almandine $(Fe_3Al_2Si_3O_{12})$, because some $Fe^{3+}$ or $OH^-$ will be present depending upon the synthesis conditions. The use of state-of-the-art powder diffractometers and least-squares fitting programs, when combined with the use of proper internal standards (*e.g.* NBS Si), allows determination of the unit-cell constant to the fourth decimal place. Table 1 lists the best estimates for the four synthetic end-member garnets. The volume at 1 bar and 298 K needs to be modified for thermodynamic calculations at different P-T conditions and can be approximated by:

$$V_{P,T} = V_{1,298\,K}[1 + \alpha(T - 298) - \beta P] \tag{2}$$

where $\alpha$ and $\beta$ are the isobaric thermal expansion and isothermal compressibility, respectively, and are treated as constants.

The thermal expansion of the four end-member garnets has been determined by *Skinner* (1956) at temperatures between 273 and 1073 K. *Bosenick* and *Geiger* (1997) have determined the thermal expansion of synthetic pyrope and grossular and their solid solutions between 20 and 300 K. Thermal expansion is defined as:

$$\alpha = \frac{1}{V_{1,298\,K}} \left(\frac{\partial V}{\partial T}\right)_P \tag{3}$$

Skinner's data were fitted to the equation (*Pawley* et al., 1996):

$$V_{1,T}/V_{1,298\,K} = 1 + \alpha_0(T - 298) - 2\alpha_1(\sqrt{T} - \sqrt{298}) \tag{4}$$

where $\alpha = \alpha_0 - \alpha_1 T^{-1/2}$. Equation (4) does not overfit the data and allows extrapolation to higher temperatures. The least-squares best fit values of $\alpha_0$ and $\alpha_1$ are given in Table 2. A plot of the $V_{1,T}/V_{1,298\,K}$ versus T is shown in Fig. 2.

Table 1. *Unit-cell constants and molar volumes of the end-member aluminosilicate garnets*

| Garnet | $a_0$ (Å) | $V_{1,298\,K}$ (J/bar) |
|---|---|---|
| Pyrope[1] | 11.4553(5) | 11.3157(16) |
| Almandine[2,3] | 11.525(2) | 11.523(6) |
| Spessartine[3,4] | 11.615(1) | 11.796(3) |
| Grossular[1] | 11.8510(5) | 12.5293(16) |

[1] *Bosenick* and *Geiger* (1997), [2] *Geiger* et al. (1988), [3] *Geiger* and *Feenstra* (1997), [4] *Rodehorst* et al. (in prep)

Table 2. *Volume expansion coefficients of the end-member aluminosilicate garnets*

| Garnet | $\alpha_0$ | $\alpha_1$ |
|---|---|---|
| Pyrope | $3.8617\times10^{-5}\pm(5.1562\times10^{-7})$ | $3.2033\times10^{-4}\pm(1.1875\times10^{-5})$ |
| Almandine | $4.5281\times10^{-5}\pm(9.6145\times10^{-7})$ | $5.1873\times10^{-4}\pm(2.2236\times10^{-5})$ |
| Spessartine | $4.7098\times10^{-5}\pm(1.9229\times10^{-6})$ | $4.8319\times10^{-4}\pm(4.3982\times10^{-5})$ |
| Grossular | $3.9002\times10^{-5}\pm(8.5151\times10^{-7})$ | $3.9130\times10^{-4}\pm(1.9374\times10^{-5})$ |

fit to data of *Skinner* (1956)
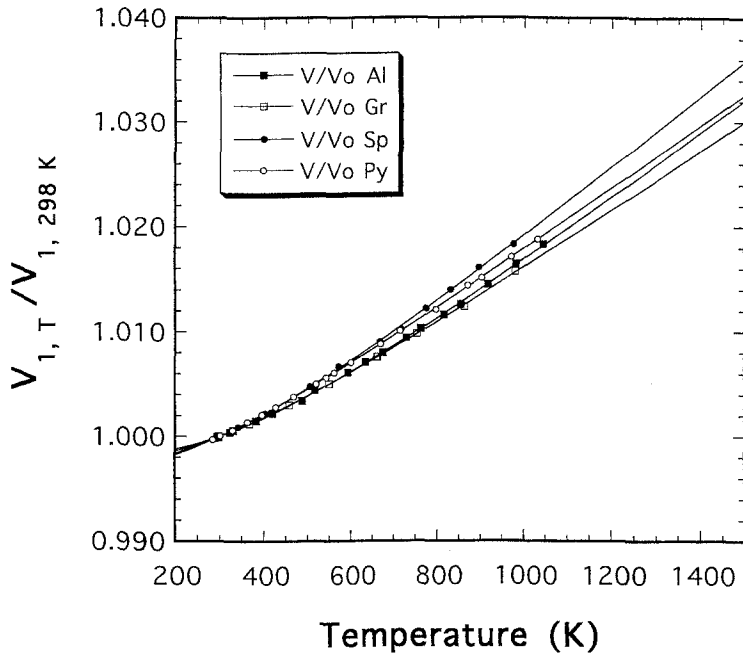


Fig. 2. Plot of the relative expansion $(V/V_0)$ between 200 and 1000 K

The change in volume of a substance as a function of pressure at constant T is described by its compressibility. It is defined as:

$$\beta = -\frac{1}{V_{1,298\,K}}\left(\frac{\partial V}{\partial P}\right)_T \tag{5}$$

The bulk modulus is frequently used in mineralogy and is defined as:

$$K_0 = \frac{1}{\beta} \tag{6}$$

where the first derivative of $K_0$ with respect to pressure is defined as:

$$K_0' = \left(\frac{\partial K_0}{\partial P}\right)_T \tag{7}$$

The relationship between pressure, volume, $K_0$, and $K_0'$ can be described by a third-order Birch-Murnaghan equation of state:

$$P = \frac{3}{2}K_0\left[\left(\frac{V}{V_{1,298\,K}}\right)^{7/3} - \left(\frac{V}{V_{1,298\,K}}\right)^{5/3}\right] \times \left\{1 - \zeta\left[\left(\frac{V}{V_{1,298\,K}}\right)^{2/3} - 1\right] + \cdots\right\}$$

(8a)

where

$$K_0' = 4 - 4/3\zeta.$$

(8b)

Both $K_0$ and $K_0'$ have been determined for a number of synthetic end-member and natural garnet solid solutions using a variety of different techniques. Brillouin spectroscopic and ultrasonic measurements provide the best determination of the elastic constants and $K_0$ at 1 bar. High-pressure single-crystal X-ray diffraction studies in the diamond-anvil cell can be used to constrain $K_0'$ and in favorable cases both $K_0$ and $K_0'$ (*Zhang* et al., in press). $K_0$ and $K_0'$ values are now known fairly well for the end-member garnets and agreement is good between the Brillouin spectroscopic and recent diamond-anvil studies. This was not the case just a few years back (see comparison of data in *Olijnyk* et al., 1991). Preferred $K_0$ and $K_0'$ values for the four end members are given in Table 3.

The four silicate garnets andradite, grossular, almandine and spessartine follow the bulk modulus-volume relationship (i.e. $K_0V^0 = $ constant) described by *Anderson* and *Anderson* (1970), whereas pyrope does not (Fig. 3). Pyrope, especially, appears to have different crystal chemical properties. This is also evidenced in some of its thermodynamic properties.

## Heat capacity and third-law entropy

Heat capacity, $C_p$, is usually measured using low-temperature adiabatic calorimetry, differential scanning calorimetry (DSC) and high-temperature drop calorimetry (or reverse drop calorimetry). The first two techniques are dynamic measuring $C_p$ as a function of temperature. The latter is a static experiment measuring the heat content at a particular temperature [$H_T-H_{298}$].

Adiabatic calorimetry delivers $C_p$ data over the temperature interval of about 10 to 380 K (*Robie* and *Hemingway*, 1972). DSC devices are generally used in the

Table 3. *Bulk moduli and its first pressure derivative of the end-member aluminosilicate garnets*

| Garnet | $K_0$ (1) (GPa) | $K_0$ (2) (GPa) | $K_0'$ (2) |
|---|---|---|---|
| Pyrope | 172.8±0.3 | 171±2 | 4.4±0.2 |
| Almandine | – | 185±3 | 4.2±0.3 |
| Spessartine | 178.8±0.8 | 183±4 | 5.1±0.6 |
| Grossular | 168.4±0.7 | 170±4 | 5.2±0.6 |

[1] *O'Neill* et al. (1991) for pyrope, *Bass* (1989) for spessartine and grossular using Brillioun spectroscopy, [2] *Zhang* et al. (in press) using diffraction methods in the diamond-anvil cell
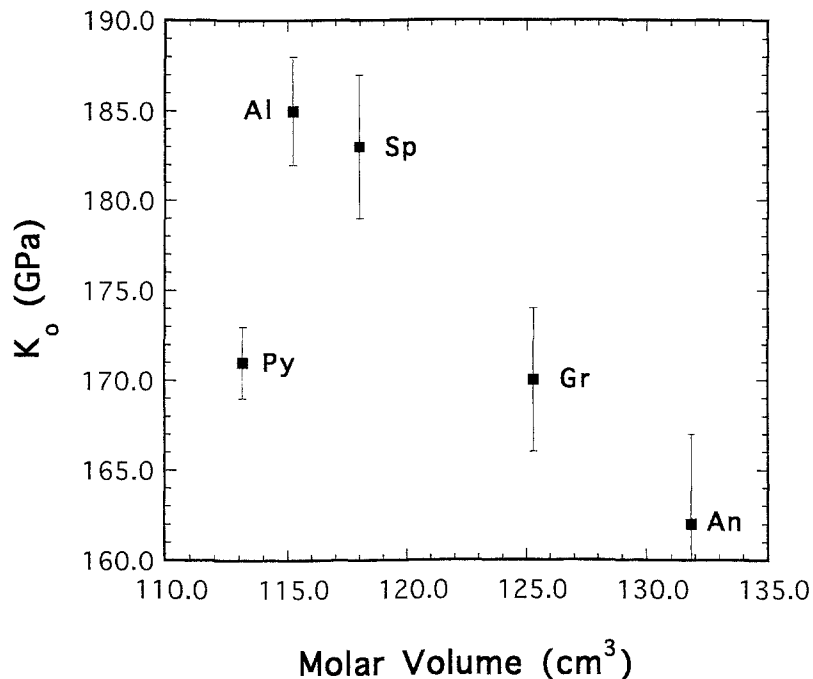
Fig. 3. Plot of the bulk moduli for the four aluminosilicate garnets and andradite versus volume

temperature interval 300 to 1000 K. Drop calorimetry is undertaken mostly at high temperatures above 1000 K. The combination of all three methods thus permits a complete coverage of the heat capacity over a large temperature interval. They permit the calculation of the third-law or lattice vibrational entropy via:

$$S_T^0 = \int_{T=0K}^{T} \frac{C_P}{T} dT \tag{9}$$

Low-temperature adiabatic calorimetry measurements have been made on synthetic end-member almandine (*Anovitz* et al., 1993), pyrope and grossular (*Haselton* and *Westrum*, 1980). DSC measurements have been made on synthetic almandine (*Anovitz* et al., 1993), pyrope (*Newton* et al., 1977a; *Watanabe*, 1982; *Bosenick* et al., 1996) [the former two references do not include data, but only present fitted $C_p$ equations], grossular (*Krupka* et al., 1979; *Bosenick* et al., 1996) and spessartine (*Geiger* and *Armbruster*, 1997). *Haselton* (1979) made reverse drop-calorimetric measurements on the same synthetic pyrope used in the low-temperature adiabatic calorimetry study.

The low-temperature $C_p$ of natural, nearly end-member grossular was measured by *Westrum* et al. (1979) and *Kolesnik* et al. (1979). *Krupka* et al. (1979) measured the $C_p$ of natural nearly end-member grossular and *Geiger* and *Armbruster* (1997) natural spessartines via DSC measurements. High-temperature drop calorimetry measurements on natural pyrope from Dora Maira have been made by *Tequi* et al. (1991). The calorimetrically determined heat capacities and standard third-law entropies at 298 K are listed in Table 4. In addition, the third-law entropies

Table 4. *Heat capacities at 298 K and standard third-law entropies of synthetic and natural nearly end-member aluminosilicate garnets*

| Garnet | $C_p^0$ J/(mole · K) | $S^0$ J/(mole · K) | $S^0$ (6) J/(mole · K) | $S^0$ (7) J/(mole · K) | $S^0$ (8) J/(mole · K) |
|---|---|---|---|---|---|
| Pyrope[1] | 325.31 | 266.27±1.51 | 274.450±0.272 | · 266.30 | 266.36 |
| Almandine[2] | 342.80±1.4 | 342.60±1.40 | 339.902±0.300 | 340.00 | 340.01 |
| Grossular[1] | 333.17 | 260.12±2.97 | 257.469±0.243 | 255.00 | 255.15 |
| Grossular[3*] | 329.41±0.84 | 254.72±0.84 | – | – | – |
| Grossular[4*] | 330.54±1.26 | 256.48±1.26 | – | – | – |
| Spessartine[5] | 342.11 | 331.499 | not listed | 367.00 | not listed |

[1]*Haselton* and *Westrum* (1980), [2]*Anovitz* et al. (1993), [3*]*Westrum* et al. (1979) natural grossular "adjusted", [4*]*Kolesnik* et al. (1980) natural grossular "adjusted", [5] *Geiger* and *Armbruster* (1997) for $C_p$ and $S^0$ from *Ottonello* et al. (1996); [6]*Gottschalk* (1997) his errors are given as $\pm 2\sigma$, [7]*Holland* and *Powell* (1998), [8]*Berman* (1991)
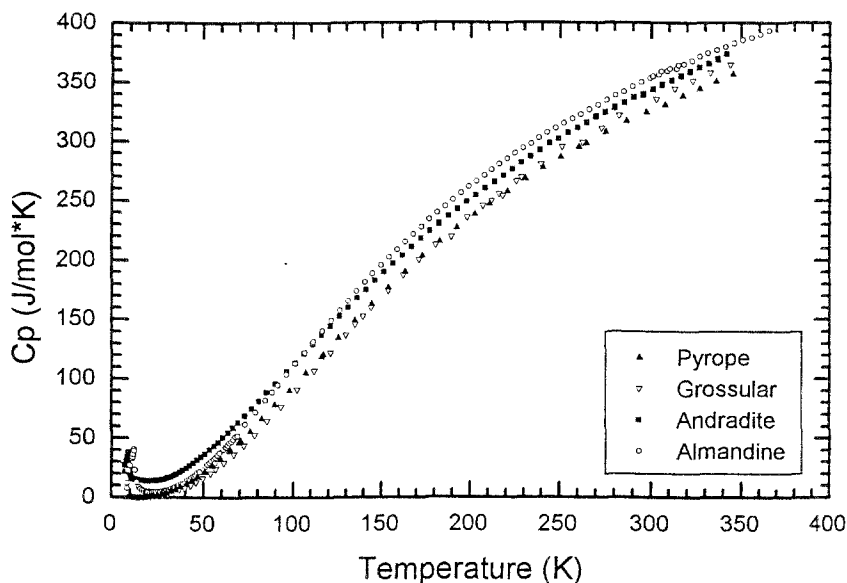


Fig. 4. Plot of the low-temperature heat capacities of pyrope, almandine and grossular measured via adiabatic calorimetry. The data are from the following sources: pyrope and grossular (*Haselton* and *Westrum*, 1980), almandine (*Anovitz* et al., 1993). Andradite is also shown for comparison (*Robie* et al., 1987)

estimated from mathematical programming analysis (*Berman*, 1991), interactive regression methods (*Gottschalk*, 1997) and weighed least-squares modeling (*Holland* and *Powell*, 1998) are listed for comparison. The agreement between calorimetry and assessments of pyrope's entropy is excellent, with the exception of the value of 274.450 J/mole·K presented by *Gottschalk* (1997).

Figure 4 shows the heat capacities for the three synthetic garnets almandine, pyrope and grossular from 10 K to 350 K. Almandine shows the presence of a lambda transition at 8.7 K resulting from a magnetic transition (*Anovitz* et al., 1993). They also concluded that an additional small entropy arises in the form of a

Schottky thermal contribution related to a disordering of the d-electrons. Both effects increase the entropy above that which would be related solely to phonons. $^{57}Fe$ Mössbauer spectra of almandine show the gradual onset of magnetic order between 10.4 and 9.6 K, with about 50% of the total spectral area being described by an ordered phase (*Murad* and *Wagner*, 1987). The spectrum in the completely magnetically ordered state at 4.2 K could be fit equally well on the basis of two different crystal chemical models, one of which allows for the existence of two crystallographically different non-equivalent X-sites (*Murad* and *Wagner*, 1987). If this is the case, then a configurational entropy contribution would have to be added to the entropy of almandine.

$S^0_{298\,K}$ of pyrope is larger than that of grossular, which has a larger molar volume and heavier mass. This results from its greater $C_p$ at low temperatures (Fig. 4). This observation has led to much discussion in the literature. Pyrope has been described as having an "anomalous" or "excess" entropy (*Charlu* et al., 1975; *Kieffer*, 1980; *Hofmeister* and *Chopelas*, 1991). It has been proposed that static spatial disordering of the Mg cation contributes to pyrope's large entropy (*Cressey*, 1981; *Hofmeister* and *Chopelas*, 1991; *Gasparik*, 1994). This explanation is not, however, entirely consistent with temperature dependent X-ray diffraction results (*Armbruster* et al., 1992; *Pavese* et al., 1995) or IR and Raman spectroscopic measurements made on pyrope (*Geiger* et al., 1992; *Kolesov* and *Geiger*, 1998), which are better explained by a strong dynamic disorder of the $Mg^{2+}$ cation.

The low-temperature adiabatic calorimetric measurements undertaken on synthetic grossular (*Haselton* and *Westrum*, 1980) and nearly end-member natural grossular (*Westrum* et al., 1979), containing 91% of a grossular component, give third-law entropies at 298 K that differ by more than 2% (Table 4). This difference is outside the error inherent to the experimental method, which is considered to be around 0.15% (*Robie* and *Hemingway*, 1972). One possible explanation for this discrepancy lies in the method used to correct for the heat capacity contributions of the solid-solution components occurring in the natural grossular. Their entropy contribution [almandine (3.8 mole%), spessartine (1.4 mole%), Mg-melanite (1.4 mole%), pyrope (0.4 mole%) and hydrogrossular (2.4 mole%)] was estimated by considering that they mix ideally. At the time of the study, experimentally determined heat capacities of almandine, spessartine, Mg-melanite and hydro-grossular were not available. In order to obtain a $S^0_T$ value for hydrogrossular an approximation had to be adopted using brucite $[Mg(OH)_2]$ as an analog. This approximation is questionable, however, considering the fundamentally different $OH^-$ structural sites in brucite compared to those in hydrogrossular. *Kolesnik* et al. (1979) also measured the low-temperature heat capacity of a natural nearly end-member grossular. It has a slightly higher third-law entropy, overlapping the value for synthetic grossular (Table 4). Heat-capacity measurements on hydro-grossular could perhaps resolve these discrepancies. It should be noted further, however, that grossular's third-law entropy obtained from modeling gives a lower value in better agreement with the measurements on the natural materials. Careful calorimetric work is required to clarify these small but important discrepancies.

There are, to date, no low-temperature heat capacity measurements on spessartine and, hence, its third-law entropy can not be obtained directly. *Geiger* and *Armbruster* (1997) argued that its lattice entropy should be similar to that of
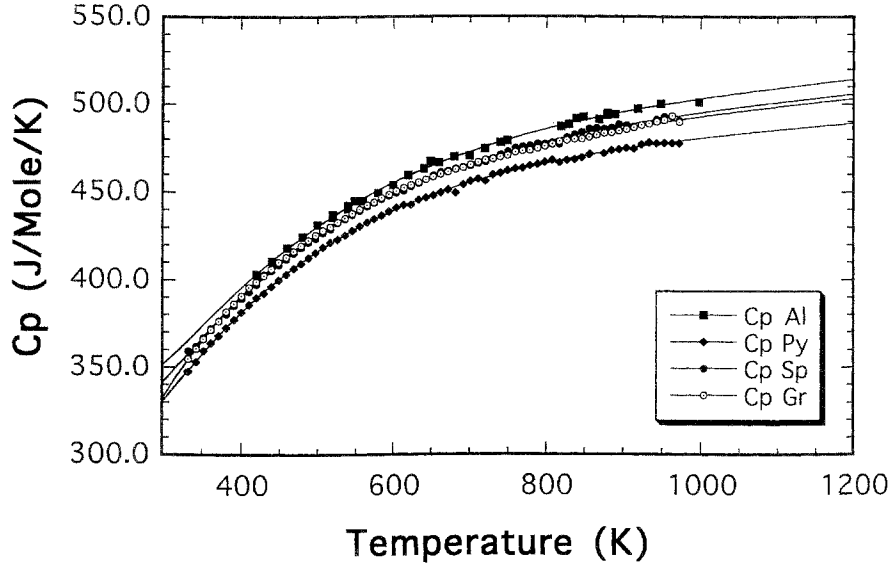
Fig. 5. Plot of the heat capacities between 350 and 1000 K using differential scanning calorimetry for the four aluminosilicate garnets almandine, grossular, pyrope and spessartine. The data are from the following sources: pyrope and grossular (*Bosenick* et al., 1996), almandine (*Anovitz* et al., 1993), and spessartine (*Geiger* and *Armbruster*, 1997)

Table 5. $C_p$ functions for the aluminosilicate garnets between 350 and 1200 K

| Garnet | $C_p$ in J/Mole · K |
|---|---|
| Pyrope[1] | $C_p = 542.01 - 1387.07 \cdot T^{-0.5} - 20.492 \times 10^6 \cdot T^{-2} + 2500.67 \times 10^6 \cdot T^{-3}$ |
| Grossular[1] | $C_p = 607.81 - 3214.49 \cdot T^{-0.5} - 12.141 \times 10^6 \cdot T^{-2} + 1269.92 \times 10^6 \cdot T^{-3}$ |
| Almandine[2] | $C_p = 573.96 - 1483.13 \cdot T^{-0.5} - 29.292 \times 10^6 \cdot T^{-2} + 5022.08 \times 10^6 \cdot T^{-3}$ |
| Spessartine[3] | $C_p = 566.73 - 1554.80 \cdot T^{-0.5} - 26.830 \times 10^6 \cdot T^{-2} + 4374.80 \times 10^6 \cdot T^{-3}$ |

[1]*Bosenick* et al. (1996), [2]fit to data of *Anovitz* et al. (1993), [3]refit to data of *Geiger* and *Armbruster* (1997)

almandine. Estimates of $S^0_{298K}$ from lattice energy calculations (*Ottonello* et al., 1996) and modeling (*Holland* and *Powell*, 1998) are given in Table 4.

Heat capacities of the four synthetic garnets in the temperature range from 350 K to 1000 K as determined by DSC measurements are shown in Fig. 5. $C_p$ equations of the type recommended by *Berman* (1988) for this temperature interval are given in Table 5. $C_p$ polynomials were fit to the data of *Anovitz* et al. (1993) for almandine and the data for synthetic spessartine (*Geiger* and *Armbruster*, 1997) after removing three data points that are considered spurious. The $C_p$-polynomials for pyrope and grossular are from *Bosenick* et al. (1996).

*Enthalpy of formation of garnet end-members*

The enthalpy of formation, $H^0_f$, of the aluminosilicate garnets from the oxides, with the exception of spessartine, have been determined by high-temperature oxide-melt

Table 6. *Enthalpies of formation from the oxides and the elements at 298 K*

| Garnet | Calorimetry $H_f^0$ (kJ/Mole) | Calorimetry $H_f^0$ (kJ/Mole) | $H_f^0$ (4) (kJ/Mole) | Modelling $H_f^0$ (5) (kJ/Mole) | $H_f^0$ (6) (kJ/Mole) |
|---|---|---|---|---|---|
| Pyrope[1] | $-78.20\pm1.59$ | $-6290.47$ | $-6280.19\pm0.75$ | $-6284.23\pm2.5$ | $-6284.74$ |
| Grossular[2] | $-320.53\pm2.80$ | $-6633.60$ | $-6632.18\pm0.78$ | $-6644.07\pm3.2$ | $-6632.86$ |
| Almandine[3] | $-53.76\pm5.10$ | $-5277.70$ | $-5265.23\pm0.71$ | $-5263.65\pm2.6$ | $-5265.44$ |
| Spessartine | no data | | $-$ | $-$ | $-$ |

[1]*Charlu* et al. (1975), [2]*Charlu* et al. (1978), [3]*Chatillon-Colinet* et al. (1983), [4]*Gottschalk* (1997) – his errors are given as $\pm2\sigma$, [5]*Holland* and *Powell* (1998), and [6]*Berman* (1991)

solution calorimetry. The technique has been described and was first applied in the mineralogical community by *Kleppa* and coworkers (*Kleppa*, 1976) and is the primary calorimetric method for obtaining enthalpy of formation data on silicates. Enthalpies of formation have also been estimated from phase equilibrium experiments and calorimetry by a number of workers. Table 6 lists the values from calorimetry and those determined from modeling. Agreement between the model values is good except for grossular. The calorimetric value for almandine is not in good agreement with those from modeling.

Estimates of $H_f^0$ obtained from modeling phase equilibrium experiments should be superior, because they are based on a large number of input data. Moreover, the calorimetrically determined values can be beset by experimental problems (e.g. oxidation or reduction of iron-containing phases, incomplete dissolution of component oxides like MgO, and uncertainties in the value of the heat of solution of CaO). Further calorimetric work is required to obtain better and more refined $H_f^0$ values and the first data on spessartine.

## Thermodynamic properties of the binary solid solutions

An understanding of the thermodynamic behavior of the four component system $Fe_3Al_2Si_3O_{12}$-$Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$-$Mn_3Al_2Si_3O_{12}$ requires a description of the mixing properties of six binary solid solutions, four ternary solid solutions and lastly, the mixing behavior within the quaternary (Fig. 1). The equation analogous to (1) for a solid solution is given by:

$$\Delta G_{P,T}^{mix} = \Delta H_{1,298\,K}^{mix} - T\Delta S_{1,298\,K}^{mix} + \int_{298\,K}^{T} \Delta C_P^{mix} dT - T\int_{298\,K}^{T} (\Delta C_P^{mix}/T) dT$$

$$+ \int_1^P \Delta V_{P,T}^{mix} dP \tag{10}$$

Here care must be used in formulating $\Delta S^{mix}$, which now contains a configurational term in addition to the lattice entropy of mixing. For a two-component solid solution it is given by:

$$S^{conf} = -zR(X_A \ln X_A + X_B \ln X_B) \tag{11}$$

where z is the number of sites over which mixing occurs, R the gas constant and $X_i$ the mole fraction of the mixing component in the solid solution. A consideration of the configurational entropy is important for part of the discussion that will follow.

The real mixing behavior can be described in terms of its relation to ideal thermodynamic mixing. The excess Gibbs free energy of mixing is defined as:

$$\Delta G^{xs} = \Delta G^{mix,\,real} - \Delta G^{id} \tag{12}$$

where $\Delta G^{xs}$ describes the deviation between the real, experimentally determined mixing behavior, $\Delta G^{mix,\,real}$, and ideal mixing, $\Delta G^{id}$. $\Delta G^{xs}$ can be described by a regular or subregular solution model (e.g. *Hildebrand* et al., 1970):

$$\Delta G^{xs} = W^G X_i X_j \tag{13}$$

$$\Delta G^{xs} = (W^G_{i,j} X_j + W^G_{j,i} X_i) X_i X_j \tag{14}$$

respectively, where $W^G$ is defined as an interaction parameter. Analogous expressions hold for the excess enthalpy of mixing, $\Delta H^{xs}$, the excess lattice entropy of mixing, $\Delta S^{xs}$, and the excess volume of mixing, $\Delta V^{xs}$.

## Volumes of mixing

The volume of mixing, $\Delta V^{mix}$, is the easiest of the thermodynamic properties to determine experimentally. The $\Delta V^{mix}$ of all six binary solid solutions has been determined and the best estimates are summarized in Table 7. The almandine-pyrope join is for all practical purposes ideal (*Geiger* and *Feenstra*, 1997), but a careful redetermination on garnets synthesized from homogeneous glasses containing no $Fe^{3+}$ could reveal very small positive asymmetric excess behavior. The almandine-spessartine, pyrope-spessartine, and spessartine-grossular joins are best described with a regular mixing model. Deviations from ideality for the first join are very small and the data from the second are preliminary. These joins are not, however, volumetrically ideal (*Hsu*, 1968; *Wood* et al., 1994; *Koziol*, 1990). The remaining two solid solutions, pyrope-grossular (*Bosenick* and *Geiger*, 1997; *Ganguly* et al., 1993) and almandine-grossular, show positive asymmetric

Table 7. *Summary of the currently estimated volume interaction parameters for three cation mixing in J/bar*

| Parameter | $W^V_{i,j}$ |
|---|---|
| Mg(Fe)-Fe(Mg)[1] | 0 |
| Fe(Mn)-Mn(Fe)[1] | 0.024±0.005 |
| Ca-Mg[2] | 0.012±0.026 |
| Mg-Ca | 0.184±0.028 |
| Fe-Ca[3] | 0.157±0.044 |
| Ca-Fe | 0.099±0.040 |
| Ca(Mn)-Mn(Ca)[4] | 0.065±0.020 |
| Mg(Mn)-Mn(Mg)[5] | 0.038±0.012 |

[1]*Geiger* and *Feenstra* (1997); [2]*Bosenick* and *Geiger* (1997); [3]This work; [4]*Rodehorst* et al. (in prep); [5]*von Saldern* (1994)

deviations from ideality. The data of *Geiger* et al. (1987) and *Cressey* et al. (1978) were used for the latter binary, but the parameters in Table 7 must be considered the best current estimation, because some of the garnets were compositionally inhomogeneous and because the effect of $Fe^{3+}$ was not rigorously ascertained. For both joins, it should be stated that any volume changes depending on the degree of short-range X-site cation order, as found in pyrope-grossular solid solutions (*Bosenick* et al., 1995; in press), have not been considered and, therefore, the P-T synthesis conditions have been ignored. Indeed, short-range order may turn out to play a role in influencing $\Delta V^{mix}$ and this aspect requires further investigation (see below). Some discrepancies or confusion in the literature regarding $\Delta V^{mix}$ behavior may be related to this effect (*Bosenick* et al., in press). For example, it has been reported in some studies on pyrope-grossular garnets that negative deviations are present in pyrope-rich compositions (see *Bosenick* and *Geiger*, 1997, for a review of the various studies). This may be the case and could reflect a relatively ordered structural state.

There are little to no data on thermal expansion and compressibility (or $\Delta V^{mix}$ at different temperatures and pressures) for binary solid solutions. *Bosenick* and *Geiger* (1997) investigated the thermal expansion of pyrope-grossular solid solutions at low temperatures (20–300 K). Within the precision of the measurements, no change in $\Delta V^{mix}$ behavior with changing temperature was observed. Measurements on the compressibilities of a well-characterized aluminosilicate garnet solid solution series have not been attempted to date. *Bass* (1986) presented data indicating that the change in $K_0$ between uvarovite and andradite is not linear, but instead shows negative deviations across the join. Here mixing involves $Fe^{3+}$ and $Cr^{3+}$ on the octahedral site. Precise Brillioun or ultrasonic measurements on a binary series could open up an interesting avenue of investigation, because volume and entropy can be related thermodynamically. The thermodynamic relationship between compressibility and thermal expansion is given by:

$$\frac{\alpha}{\beta} = \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{15}$$

A determination of the compressibilities of a series of pyrope-grossular garnets could give important information on the entropies of mixing as a function of volume.

*Heat capacities and vibrational lattice entropies of mixing*

There is a critical dearth of data on the heat capacities or vibrational third-law entropies of mixing, $\Delta S^{mix}$, of garnet solid solutions (this holds also for silicate solid solutions in general). The reasons for this are mainly two fold. First, there are little calorimetric data because of the time consuming and arduous work involved in the synthesis of sufficient amounts of material for measurement (i.e. adiabatic calorimetry requires around 5–10 grams of material and the production of such large amounts using high-pressure synthesis methods is difficult, if not prohibitive). Second, although it is, in principle, possible to retrieve $\Delta S^{mix}$ from reversed phase equilibrium data, such experiments have contributed little quantitative and

definitive information. This is because most phase equilibrium studies are made over a limited range of composition (e.g. *Hensen* et al., 1975) and/or over a limited range of temperature. The latter fact often leads in modeling attempts in extracting entropic and enthalpic terms from the Gibbs free energies of mixing to over-estimates of both. This is probably the case for model estimates of the mixing properties of almandine-grossular (*Cressey*, 1981) and pyrope-grossular garnets (*Gasparik*, 1984) derived from phase equilibrium experiments. Both studies report large positive $\Delta H^{xs}$ and $\Delta S^{xs}$. This is required in order to obtain nearly ideal $\Delta G^{mix}$ behavior at high temperatures. The mixing models of *Mukhopadhyay* et al. (1997), which in the case of almandine-bearing solid solutions are very asymmetric, may have similar correlation effects between $\Delta H^{xs}$ and $\Delta S^{xs}$.

*Haselton* and *Westrum* (1980) undertook the only low-temperature calorimetric heat-capacity investigation for a binary garnet solid solution, namely pyrope-grossular, thus enabling the vibrational $\Delta S^{mix}$ to be determined directly. Measurements made in the temperature range 10-350 K on synthetic pyrope, grossular and one solid-solution composition, $pyrope_{60}grossular_{40}$, show that substantial $\Delta C_p^{xs}$ (i.e. excess vibrational entropy of mixing) exists. The measurements show that the $\Delta C_p^{xs}$ originates largely below 120 K. The $\Delta S^{xs}$ at 298 K for this binary, fitting the single datum with a regular solution model, gives an interaction parameter of $W^S = 18.8$ J/mole·K. In order to test the possibility that nonideality might exist at higher temperatures, the heat capacities of five synthetic pyrope-grossular solid-solution compositions were measured using DSC methods between 350 K and 1000 K (*Bosenick* et al., 1996). Within the precision of the measurements (±1%), no deviation from ideality could be detected. This suggests that the other garnet solid solutions should also have ideal $\Delta C_p^{mix}$ in this temperature range.

The most recent estimates for $\Delta S^{xs}$, based primarily on phase equilibrium data for three binary solid solutions, are compiled in Table 8. *Ganguly* et al. (1996) and *Berman* and *Aranovich* (1997) consider the different binaries to have positive symmetric or ideal behavior, while *Mukhopadhyay* et al. (1997) present asymmetrical mixing models. It would be surprising, from both thermodynamic and crystal chemical reasoning, in for example the pyrope-grossular binary, that both $\Delta V^{xs}$ and $\Delta H^{xs}$ are asymmetric, but $\Delta S^{xs}$ symmetric. It should be the case that $\Delta V^{xs}$ and $\Delta S^{xs}$ have similar behavior in their deviations from ideality (e.g. *Geiger* and *Feenstra*, 1997). The agreement between the three different models in

Table 8. *Summary of entropic interaction parameters expressed using a regular or subregular model for three cation mixing in J/mole · K*

| Parameter | $W_{i,j}^S$ (1) | $W_{i,j}^S$ (2) | $W_{i,j}^S$ (3) |
|---|---|---|---|
| Ca-Mg | 20.82±3.23 | 17.34 | 18.79 |
| Mg-Ca | 2.49±5.16 | 17.34 | 18.79 |
| Fe-Ca | 14.51±9.58 | 5.07 | 9.43 |
| Ca-Fe | −15.51±8.14 | 5.07 | 9.43 |
| Fe-Mg | −22.09±1.92 | 0 | 4.11 |
| Mg-Fe | 12.40±1.80 | 0 | 4.11 |

(1) *Mukhopadhyay* et al. (1997), (2) *Ganguly* et al. (1996) and (3) *Berman* and *Aranovich* (1996)

Table 8 and others in the literature is not very good and reveals both the weaknesses inherent in the thermodynamic modeling presently being undertaken (see below) and a lack of the necessary data needed to constrain the mixing properties.

There is one low-temperature heat capacity determination of a natural pyrope-rich garnet of composition $Py_{70.3}Al_{19.5}Gr_{8.2}An_{2.1}$ (*Kolesnik* et al., 1977). Its standard vibrational entropy of 276.35 J/mole $\cdot$ K can be compared to a value of 281.97 J/mole $\cdot$ K, which can be calculated assuming ideal mixing with the $S^0_{298\,K}$ values in Table 4 (the standard entropy of andradite is $316.4\pm2.0$ J/mole $\cdot$ K, *Robie* et al., 1987). If the various $S^0_{298\,K}$ values are correct, then this pyrope-rich solid solution has a negative deviation from ideal mixing.

*Enthalpies of mixing*

The enthalpies of mixing, $\Delta H^{mix}$, of three binaries have been experimentally determined by high-temperature oxide melt solution calorimetric techniques. The three solid solutions are pyrope-grossular (*Newton* et al., 1977b), almandine-grossular and almandine-pyrope (*Geiger* et al., 1987). In addition, there have been a number of attempts made to estimate $\Delta G^{mix}$ and/or $\Delta H^{mix}$ through an analysis of element partitioning data on both natural and synthetic mineral pairs (e.g. *Ganguly* and *Saxena*, 1984; *Koziol* and *Bohlen*, 1992; *Wood* et al., 1994), through "displaced reaction" phase-equilibrium studies (*Ganguly* and *Kennedy*, 1974; *Hensen* et al., 1975; *Cressey* et al., 1978; *Wood*, 1988; *Koziol*, 1990; *Ganguly* et al., 1996) or statistical/mathematical treatment of experimental data (e.g. *Berman* and *Aranovich*, 1996; *Mukhopadhyay* et al., 1997).

Many estimates of $\Delta H^{xs}$ have been presented in the literature. Three of the most recent are compared in Table 9. The agreement between them is fair to poor. The disagreement over the almandine-pyrope join is especially discouraging considering the petrological and geophysical importance of this binary. Estimates of the mixing properties which rely heavily upon phase equilibrium investigations are very model dependent and involve a number of assumptions [e.g. the determination of the mixing properties of one phase depend critically upon the mixing properties adopted for the coexisting phase(s)]. Moreover, the compositional ranges that are investigated in many experiments are often restricted (see however, *Cressey* et al., 1978). Hence, it is difficult to formulate mixing models

Table 9. *Summary of enthalpic interaction parameters expressed using a regular or subregular model for three cation mixing in J/mole*

| Parameter | $W^H_{i,j}$ (1) | $W^H_{i,j}$ (2) | $W^H_{i,j}$ (3) |
|---|---|---|---|
| Ca-Mg | $65182\pm2786$ | 64881 | 68280.00 |
| Mg-Ca | $14306\pm3714$ | 29502 | 33470.00 |
| Fe-Ca | $17526\pm11672$ | 20319 | 21951.40 |
| Ca-Fe | $-18113\pm10064$ | 2619 | 11581.50 |
| Fe-Mg | $-24166\pm2657$ | 2085* | 5064.50 |
| Mg-Fe | $22265\pm2487$ | 6351* | 6249.10 |

(1) *Mukhopadhyay* et al. (1997), (2) *Ganguly* et al. (1996) and (3) *Berman* and *Aranovich* (1996), * from *Hacker* and *Wood* (1989)

covering the whole compositional range of a binary solid solution. In addition, at least in the case of garnet, there are severe difficulties in obtaining equilibrium reaction reversals in exchange experiments undertaken at temperatures less than 1000 °C (*Pattison*, 1994).

The calorimetric measurements also have their drawbacks. The errors associated with the use of the $(Li,Na)BO_2$ solvent, which is needed for almandine-containing solid solutions, are large and it was not possible to obtain precise estimates of $\Delta H^{mix}$ for the almandine-pyrope/grossular joins (*Geiger* et al., 1987). The effect of structural state on the heat of solution is also not known (i.e. short-range ordering in the case of the pyrope-grossular solid solutions). New calorimetric measurements employing better characterized materials and improved methods are needed on all binaries.

## Discussion

With the exception of spessartine, the thermodynamic properties of the four end-member garnets are now well known. On the other hand, a quantitative description of the mixing properties is presently not available. This is evidenced after a quick pursual of the literature, where one is confronted with conflicting thermodynamic mixing models. It is not the intention herein to try to sort out the discrepancies. The author is convinced that better understanding will only be reached by further experimental studies and not by reanalyzing previous data. Theoretical investigations on solution models are also urgently needed. The solution models that are presently used for silicates are largely empirical in nature (see *Hildebrand* et al., 1970). Their physical basis is limited. Hence, only little work has been done in the way of trying to understand from a microscopic point of view the macroscopic thermodynamic mixing behavior, and there exists a tremendous need for theoretical work in this area. We consider below the crystal-chemical and microscopic properties which affect or control the macroscopic mixing properties.

*Volumes of mixing*

The $\Delta V^{mix}$ behavior of the binaries can be described through an analysis of the static crystal chemical behavior of the garnet structure with changing X-site composition (*Born* and *Zemann*, 1964; *Ungaretti* et al., 1995; *Geiger* and *Feenstra*, 1997). Specifically, a nonlinear change in the degree of tetrahedral rotation (Fig. 6) is considered to play a major role in $\Delta V^{mix}$ behavior along the pyrope-grossular binary. The almandine-pyrope binary shows, in contrast, a linear change in the angle of rotation between almandine and pyrope (*Armbruster* et al., 1992). The former join is characterized by positive asymmetric deviations from ideality and the latter by ideal $\Delta V^{mix}$. The $\Delta V^{mix}$ behavior can be correlated with the degree of tetrahedral rotation (*Geiger* and *Feenstra*, 1997), but internal polyhedral deformation also occurs, because of the large number of shared polyhedral edges in garnet. *Ungaretti* et al. (1995) modeled the $\Delta V^{mix}$ of pyrope-grossular and almandine-pyrope solid solutions using as input data the results of 281 single-crystal X-ray structure refinements. They calculate symmetric positive deviations for the former binary and small positive asymmetric deviations for the latter. They
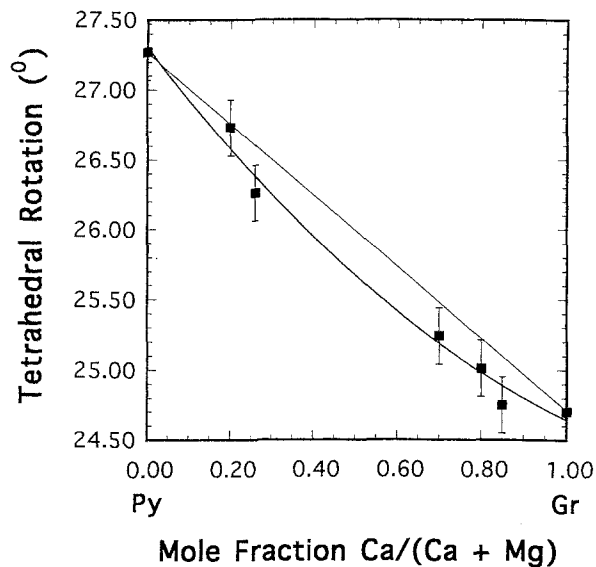
Fig. 6. Tetrahedral angle of rotation calculated for synthetic pyrope-grossular garnets using the Rietveld refinement data of *Ganguly* et al. (1993). The curved line is a third-order polynomial fit to the data
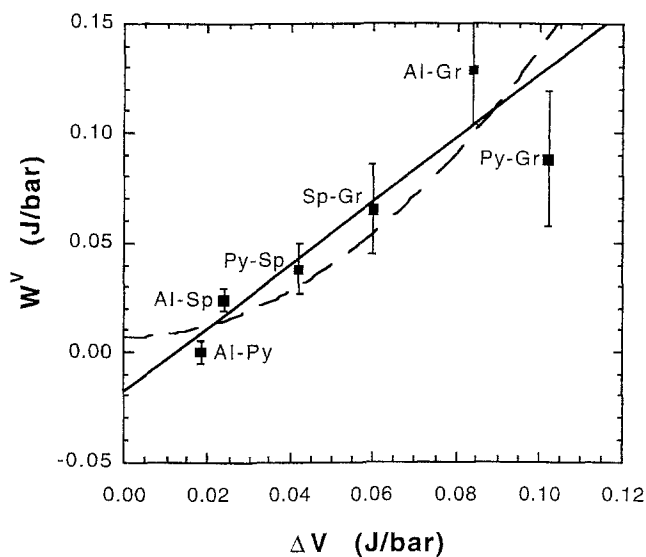


Fig. 7. Plot of the deviation from ideality in the volumes of mixing expressed using a regular solution model versus the differences in molar volumes of the two end-member garnets. The data for the almandine-grossular binary are from *Cressey* et al. (1978), *Geiger* et al. (1987), and *Koziol* (1990) and for the pyrope-grossular binary from *Newton* et al. (1977b), *Haselton* and *Westrum* (1980), *Delany* (1981), *Wood* (1988), *Ganguly* et al. (1993), and *Bosenick* and *Geiger* (1997)

place an emphasis on bonding differences between calcic and noncalcic garnets and site distortion of the three different polyhedra in controlling the mixing properties.

The present experimental data now permit an analysis of the crystal-chemical properties which cause deviations from ideality. Figure 7 shows a plot of $W^v$ for the

six binaries, as described by a regular solution fit (a regular fit for all the binaries was adopted because all published data for the pyrope-grossular and almandine-grossular binaries were used, which results in relatively large scatter), versus the volume difference between the two garnet endmembers (*Geiger*, submitted). A linear function can be fit to the data:

$$W^v(J/bar) = 1.458(\pm0.229)\Delta V - 0.019(\pm0.007) \qquad (16a)$$

A second fit can be made by fitting a quadratic equation given by:

$$W^v(J/bar) = 0.007(\pm0.004) + 13.146(\pm2.239)\Delta V^2 \qquad (16b)$$

A similar analysis of the nonideality in the Gibbs free energy of mixing of different solid solutions was made by *Davies* and *Navrotsky* (1983). An analysis of Fig. 7 suggests that strain resulting from the substitution of cations of different size is mainly responsible in causing the volumes to deviate from ideality. Hard Mode IR spectroscopic measurements made on the three garnet binaries pyrope/ almandine-grossular and almandine-pyrope demonstrate that local distortions occur over length scales of at least 5 to 150 Å (*Boffa Ballaran* et al., in press). Local structural heterogenities exist and are greatest in pyrope-grossular garnets and least in pyrope-almandine solid solutions. They are large in almandine-grossular garnets, but less than the pyrope-grossular series. The data suggest a ratio between the volumes of mixing of pyrope-grossular to almandine-grossular of approximately 1.4:1. Considering the experimental uncertainties in the volumes, especially in those of the latter, we think this possible. More importantly, there is good agreement between the range of local distortions on a microscopic scale and the macroscopic strain recorded in the volumes of mixing.

Here much depends upon the nature of the X-site and the degree of local relaxation around it which occurs upon mixing. Local-bond behavior in garnet, or in silicate solid solutions in general, is poorly understood. Results on semi-conductor solid solutions can act as a useful guide (*Mikkelsen* and *Boyce*, 1983; *Martins* and *Zunger*, 1984). Figure 8 shows the possible behavior of the two crystallographically independent local X-site cation lengths in pyrope-grossular solid solutions. The Mg-O and Ca-O bond lengths probably do not change continuously between their values in pyrope and grossular (see *Ganguly* et al., 1993 and *Ungaretti* et al., 1995), respectively (i.e. the virtual crystal approximation as determined in a diffraction experiment), but instead retain to a large degree the distances that they posses in their respective end-member compositions. Thus, Ca sites in pyrope-rich compositions should be relatively compressed, generating locally high strain. Mg cations in grossular-rich compositions should have increased amplitudes of vibration, which are already strong and highly anisotropic in pyrope (*Armbruster* et al., 1992). EXAFS measurements on the Mg and Ca edges made on a series of pyrope-grossular garnets are needed to test this hypothesis. It can be stated that the Mössbauer isomer shifts associated with $Fe^{2+}$, which is similar in size to Mg, in almandine-grossular solid solutions do not change as a function composition (*Geiger* et al., 1990) indicating, at least to a first degree, that $Fe^{2+}$ does not change its bonding character with increasing grossular content in garnet. The implications for such local-bond behavior are important, because if the virtual crystal approximation is not correct, it will not be possible to model or
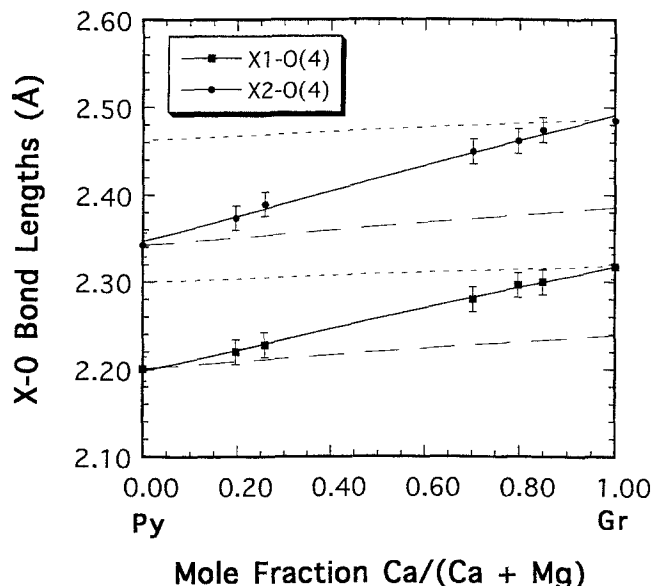
Fig. 8. The two crystallographically independent X-ray diffraction determined (Ca,Mg)-O bond lengths in synthetic pyrope-grossular solid solutions (data taken from *Ganguly* et al., 1993) as shown by the solid lines. This is the virtual crystal approximation. The different dashed lines show the possible local Mg-O and Ca-O bond lengths as a function of composition. They should only be slightly dependent on garnet bulk composition. Effects related to the excess volume properties are considered to be secondary in nature and have been ignored

calculate the thermodynamic properties of garnet solid solutions through mean-field approximations (*Bosenick* et al., in prep).

*Enthalpies of mixing*

It is not the intent to review the various thermodynamic solution models applied to silicate solid solutions here, as this has been done amply in the past (e.g. *Fei* et al., 1986). However, insight into energetic processes can be learned from the existing thermodynamic and crystal chemical data and presently available solutions models. A consideration of microscopic and macroscopic properties must be done, because any thermodynamic formulation must have a reasonable physical interpretation or be consistent with known crystal-chemical properties. For example, the asymmetric mixing models of *Mukhopadhyay* et al. (1997) presuppose that strong Fe-Mg/Ca interactions are present in pyrope- and almandine-rich compositions, respectively, which should lead to some type of compound formation or long-range order, which is not supported by any structural data. The pyrope-grossular join has received the most thermodynamic and crystal-chemical study and, here, the various data can be interpreted with some degree of confidence. An analysis of this binary can, therefore, serve as a basis for further study and understanding of the other solid solutions.

It is normally assumed that the energy of mixing of a solid solution, ignoring phonon effects, can be broken down into two parts, namely a strain or elastic energy and a chemical energy part (e.g. *Srivastava* et al., 1985; *Ferreira* et al., 1988). The elastic-energy contribution has been investigated in the case of pyrope-grossular garnets by *Ganguly* et al. (1993), who proposed that it generated positive deviations from ideality, but in a sense opposite to $\Delta V^{xs}$. It remains to be shown if the model (*Ganguly* et al., 1993), which was derived for simpler two phase metals (*Ferreira* et al., 1988), is applicable to silicate structures, because the strain fields in both types of solid solutions should be quite different. But it certainly offers a good starting point. Here we would like to discuss possible interactions between neighboring X-sites. One model which can be applied is the Quasi-Chemical (QC) Approximation of *Guggenheim* (1952), which accounts for nonrandom mixing of atoms. The garnet structure is, compared to other silicates, relatively well suited for analysis due to its high symmetry and because of the single dodecahedral X-site
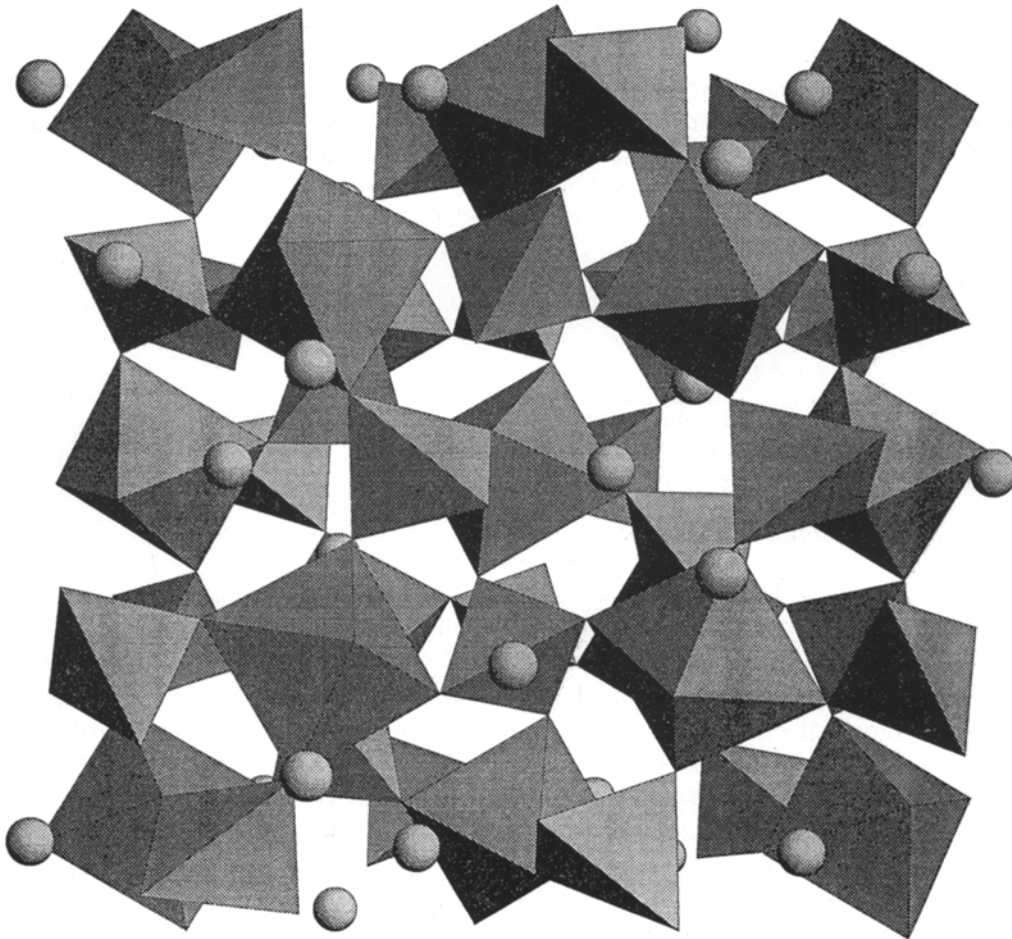


Fig. 9. Polyhedral model of the garnet structure showing the "framework" consisting of rigid corner-linked $SiO_4$ tetrahedra and $AlO_6$ octahedra. The X-site cations are found in the large dodecahedral cavities where they vibrate anisotropically in the plane of the longer X-O bonds
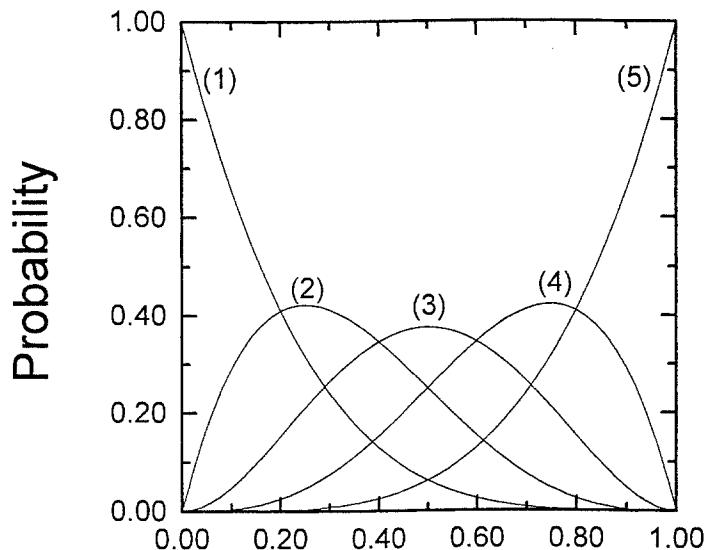
Fig. 10. Probabilities of the five possible local configurations around a given X-cation with strictly random mixing in a binary garnet solid solution as a function of composition. For example, in the pyrope-grossular solid solution there exist Mg-Mg-Mg-Mg (1), Mg-Mg-Mg-Ca (2), Mg-Mg-Ca-Ca (3), Mg-Ca-Ca-Ca (4) and Ca-Ca-Ca-Ca (5) configurations, whose individual probabilities are given by the five different curves

over which mixing occurs. It is assumed that the garnet "framework" consisting of rigid corner-sharing $SiO_4$ tetrahedra and $AlO_6$ octahedra (e.g. *Born* and *Zemann*, 1964; *Geiger* and *Feenstra*, 1997, Fig. 9) does not enter into the mixing process, which is solely governed by X-site cation interactions. Only pairwise interactions between cations in edge-sharing dodecahedra are considered to influence $\Delta H^{mix}$. The mixing of cations allows for five local configurations around a given X-site, whose probabilities for a perfectly random mixture are given by the distributions shown in Fig. 10.

The QC Model defines interaction energies between two different atoms in a solution (A,B)Y, where $\omega_{AA}$ is the interaction energy between nearest neighbor A-A atoms, $\omega_{BB}$ the energy between nearest neighbor B-B atoms and $\omega_{AB}$ the energy between A-B atoms. The excess enthalpy, $\Delta H^{xs}$, can be expressed by:

$$\Delta H^{xs} = \frac{1}{2} N z X_A X_B [2\omega_{AB} - \omega_{AA} - \omega_{BB}]$$ (19)

When the term in brackets is equal to zero there is ideal mixing (i.e. $\Delta H^{xs} = 0$). When $[2\omega_{AB} - \omega_{AA} - \omega_{BB}]$ is greater than zero, the energy of two A-B interactions is greater than the sum of one A-A and one B-B interaction, giving a positive $\Delta H^{xs}$. This suggests that A-A and B-B interactions should be energetically favored (i.e. pair formation or short-range order). If the term in brackets is less than zero, than $\Delta H^{xs}$ is negative and compound formation will be expected, because the energy of two A-B interactions is less than the sum of one A-A and one B-B interaction.

The $\Delta H^{xs}$ for the pyrope-grossular binary are positive (*Newton* et al., 1977b) implying that Mg-Mg and Ca-Ca interactions could be energetically favored (the

calorimetrically determined enthalpy contains, of course, both strain and chemical effects). This possibility is borne out by $^{29}Si$ NMR spectroscopic studies, which have shown that microscopic pyrope-rich like domains or clusters and grossular-rich clusters occur in larger concentrations than those given by a random distribution (Fig. 10) in compositions in the middle part of the join (*Bosenick* et al., 1995; submitted). It should be emphasized that this ordering is local and not long range and cannot be detected by conventional diffraction methods. *Haselton* and *Newton* (1980) and *Ganguly* et al. (1996) have calculated the T-X phase diagram for the pyrope-grossular join showing that a solvus is present (whose $T_c$ is at either 1000 °C or 600 °C at 40 kbar, according to the respective estimates). Thus, short-range ordering of Mg and Ca into pyrope- and grossular-like clusters at temperatures above $T_c$ is to be expected prior to exsolution at lower temperatures. This analysis based on the QC model considers only local pairwise interactions, which is a simple approximation and not strictly held in solid solutions. Interactions are not restricted to nearest neighbors and the model, therefore, only offers a starting point for further investigations.

It is generally thought, as in the case of semiconductor solid solutions (e.g. *Srivastava* et al., 1985), that strain effects are predominant over chemical effects in determining $\Delta H^{mix}$ (e.g. *Davies* and *Navrotsky*, 1983). For example, the maximum excess elastic energy calculated by *Ganguly* et al. (1993) is around 3 KJ/mole in the case of pyrope-grossular garnets, whereas crystal field stabilization energies of $Fe^{2+}$ in Al-Py or Al-Sp solid solutions lie between $-0.2$ and $-0.8$ KJ/mole (*Geiger* and *Rossman*, 1994). There exists little information on microscopic strain fields which occur in silicate solid solutions. Strain fields are fairly localized and decay exponentially from the site of substitution with a $1/R^n$ relationship, where $n \geq 3$ (e.g. *Bratkovsky* et al., 1996).

A difficulty in trying to interpret rigorously $\Delta H^{mix}$ energetics lies in describing X-site interactions. It should be possible to calculate the energy associated with each local-cation configuration and together with their probabilities (Fig. 10) to calculate the energy of mixing for a given bulk composition. It should also be possible to determine which configurations are energetically favored in the case of short-range order. Static lattice energy calculations using transferable potentials are starting in this direction and have revealed interesting possibilities (*Bosenick* et al., in prep.). They show, for example, that it is energetically unfavorable to place either two Mg cations into an edge-shared dodecahedral-tetrahedral-dodecahedral arrangement in a grossular-rich host or to place two such Ca cations in a pyrope-rich host. The energetics do not appear to be unfavorable regarding the placement of Ca or Mg cations next to each other in edge-shared dodecahedra.

## Entropies of mixing

Little can be said about the vibrational entropies of mixing because of lack of data. The present confusion and uncertainty, for example, are best illustrated by the various $\Delta S^{xs}$ models proposed for almandine-pyrope garnets (Fig. 11). *Mukhopadhyay* et al. (1997) propose negative $\Delta S^{xs}$, which should lead to increasing positive $\Delta G^{xs}$ with increasing temperature. It appears that $\Delta S^{xs}$, where they do exist, are originating at low temperatures (*Haselton* and *Westrum*, 1980;
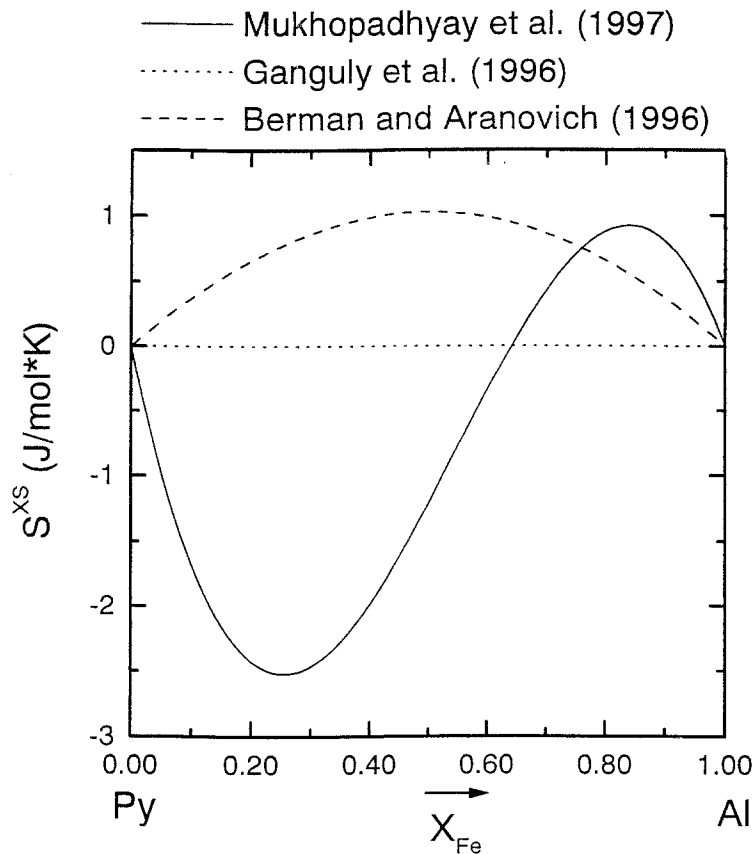
Fig. 11. Plot of $\Delta S^{xs}$ of almandine-pyrope garnets as estimated from three thermodynamic studies on garnet solid solutions, *Mukhopadhyay* et al. (1997), *Ganguly* et al. (1996) and *Berman* and *Aranovich* (1996)

*Bosenick* et al., 1996). Moreover, based on crystal-chemical considerations, it is to be expected that in those cases where $\Delta V^{xs}$ show positive deviations from ideality, then $\Delta S^{xs}$ may also be positive (*Geiger* and *Feenstra*, 1997). This proposal is supported by simple lattice-dynamic considerations based on the Raman and IR spectra of garnet solid solutions (*Kolesov* and *Geiger*, 1998; *Geiger*, 1998). It follows from these studies that the Al-Sp binary should be nearly entropically ideal, the Al-Gr and Sp-Gr should have relatively large deviations from ideality and the Al-Py and Py-Sp binaries could have measurable deviations from ideality. Besides the $C_p$ results on the pyrope-grossular join, no other heat capacity data exist for a binary solid solution and hence, these proposals remain to be tested.

Phonon effects, which may not be so important in estimating $\Delta V^{mix}$ and $\Delta H^{mix}$, cannot be ignored in the case of the vibrational entropy. The strongly anisotropic vibrational behavior of the X-site cations in the garnet framework will have to be considered in any lattice dynamic calculations of $C_p$. In pyrope, for example, some Mg vibrations occur at very low frequencies (*Kolesov* and *Geiger*, 1998) and affect $C_p$ at low temperatures.

The configurational entropies will be poorly known, if short-range order is present. In the case of pyrope-grossular garnets ordering is present, because Mg and Ca are not completely randomly distributed on the X-site (*Bosenick* et al. 1995; in press). For garnets synthesized above 1000 °C the degree of order is not great, but is measurable. *Bosenick* et al. (in press) estimate a reduction in the configuational entropy for pyrope-rich compositions around 2 J/mole·K in the most ordered garnets. The calcualtion was done using cluster variation methods assuming 6-clusters of edge-shared dodecahedra. It remains to be determined, however, what the structural state is at lower temperatures between 600–900 °C. The degree of short-range order could be substantial in many metamorphic garnets.

## Future investigations and outlook

The state of knowledge of the mixing properties of garnet solid solutions is summarized in Table 10. Much work is required before a quantitative understanding is at hand.

Future research on garnet solid solutions, in this author's opinion, should focus on the following: 1) Precise determinations of $\Delta V^{mix}$ for the almandine-grossular and pyrope-spessartine binaries following improved synthesis (starting with homogeneous glasses) and careful characterization (e.g. $^{57}$Fe Mössbauer and IR spectroscopy) procedures. The $\Delta V^{mix}$ can be determined with great precision and accuracy, and can give important macroscopic strain information that may help in understanding $\Delta H^{mix}$. Precise molar-volume determinations on solid solutions can also give indirect information on the degree of short-range X-site cation order (e.g. *Bosenick* et al., in press). 2) Spectroscopic studies (NMR and hard mode IR measurements) focusing on short-range ordering, especially for almandine/pyrope-grossular solid solutions. It may well be that many garnet solid solutions, both synthetic and natural, have short-range order of the different X-site cations. All thermodynamic activity models assume that the X-site cations in garnet are completely disordered and thus may overestimate the configurational entropy of mixing. Theoretical work is also required in order to calculate the configurational entropies as a function of temperature in cases where short-range order is present. 3) Low-temperature $C_p$ measurements on the different garnet binaries. *Bosenick* et al. (1996) have argued that thermodynamic nonidealities in garnet solid solutions

Table 10. *Evaluation of the reliability of the mixing properties of binary garnet solid solutions. The symbols ++ mean well determined, + partially determined, but further measurements necessary, – no data or only poorly constrained*

| Binary | $\Delta V^{mix}$ | $\Delta H^{mix}$ | $\Delta S^{mix}$ |
|--------|--------|--------|--------|
| Al-Py | ++ | + | – |
| Al-Sp | ++ | – | – |
| Sp-Py | + | – | – |
| Al-Gr | + | + | – |
| Sp-Gr | + | – | – |
| Py-Gr | ++ | + | + |

are originating at low temperatures (i.e. below 200 K). For reasons stated above, it is unlikely that estimates of the vibrational $\Delta S^{mix}$ retrieved from phase equilibrium studies will yield quantitative results, because of correlation problems and the unknown effect of short-range order in influencing the total $\Delta S^{mix}$ of a system. 4) High-temperature heat of solution measurements on well-characterized binaries employing improved calorimetric methods allowing better experimental precision.

In general, the author believes that more effort has to be made on calorimetric investigations, which provide direct data on $\Delta S^{mix}$ and $\Delta H^{mix}$, versus conventional phase-equilibrium experiments. In spite of the large number of phase-equilibrium studies that have been undertaken on garnet-bearing systems, it is still the few calorimetric results which are used to pin down the mixing behavior. The single datum for the heat capacity of the one pyrope-grossular solid solution (*Haselton* and *Westrum*, 1980) is evidence for this. It should also not be forgotten that all measurements will require the synthesis of homogeneous solid-solution garnets that are well characterized in terms of their structural state, something that was not recognized or realized by experimentalists in many earlier studies.

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## References

*Anderson DL, Anderson OL* (1970) The bulk modulus-volume relationship for oxides. J Geophys Res 75: 3494–3500

*Anovitz LM, Essene EJ, Metz GW, Bohlen SR, Westrum EF Jr, Hemingway BS* (1993) Heat capacity and phase equilibria of almandine, $Fe_3Al_2Si_3O_{12}$. Geochim Cosmochim Acta 57: 4191–4204

*Armbruster T, Geiger CA, Lager GA* (1992) Single-crystal X-ray structure study of synthetic pyrope almandine garnets at 100 and 293 K. Am Mineral 77: 512–521

*Bass JD* (1986) Elasticity of uvarovite and andradite garnets. J Geophys Res 91: 7505–7516

*Bass JD* (1989) Elasticity of grossular and spessartite garnets by Brillouin spectroscopy. J Geophys Res 94: 7621–7628

*Berman RG* (1988) Internally-consistent thermodynamic data for minerals in the system $N_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2$. J Petrol 29: 445–522

*Berman RG* (1990) Mixing properties of Ca-Mg-Fe-Mn garnets. Am Mineral 75: 328–344

*Berman RG* (unpublished) Thermodynamic update

*Berman RG, Aranovich LYa* (1997) Optimized standard state and solution properties of minerals I. Model calculations for olivine, orthopyroxene, cordierite, garnet, and ilmenite in the system $FeO-MgO-CaO-Al_2O_3-TiO_2-SiO_2$. Contrib Mineral Petrol 126: 1–24

*Boffa Ballaran T, Carpenter MA, Geiger CA, Koziol AM* (1999) Local structural heterogeneity in garnet solid solutions. Phy Chem Mineral 26 (in press)

*Born L, Zemann J* (1964) Abstandsberechnungen und gitterenergetische Berechnungen an Granaten. Contrib Mineral Petrol 10: 2–23

*Bosenick A, Geiger CA* (1997) Powder X-ray diffraction study of synthetic pyrope-grossular garnets between 20 and 295 K: a comparison of thermal expansion and heat capacity and volumes of mixing. J Geophys Res 102: 22,649–22,657

*Bosenick A, Geiger CA, Schaller T, Sebald A* (1995) A $^{29}$Si MAS NMR and IR spectroscopic investigation of synthetic pyrope-grossular garnet solid solutions. Am Mineral 80: 691–704

*Bosenick A, Geiger CA, Cemic L* (1996) Heat capacity measurements of synthetic pyrope-grossular garnets between 320 and 1000 K by differential scanning calorimetry. Geochim Cosmochim Acta 60: 3215–3227

*Bosenick A, Geiger CA, Phillips BL* (1999) Local Ca-Mg distribution of Mg-rich pyrope-grossular garnets synthesized at different temperatures revealed by $^{29}$Si NMR MAS spectroscopy. Am Mineral 84 (in press)

*Bosenick A, Dove MT, Meyers E, Hammonds K, Geiger CA* (1999) Simulation studies of pyrope-grossular solid solutions (in preparation)

*Bratkovsky AM, Heine V, Salje E* (1996) Strain effects, particularly in phase transitions. Phil Trans Royal Soc Lond A 354: 2875–2896

*Charlu TV, Newton RC, Kleppa OJ* (1975) Enthalpies of formation at 970 K of compounds in the system $MgO$-$Al_2O_3$-$SiO_2$ from high temperature solution calorimetry. Geochim Cosmochim Acta 39: 1487–1497

*Charlu TV, Newton RC, Kleppa OJ* (1978) Enthalpy of formation of some lime silicates by high-temperature solution calorimetry, with discussion of high pressure phase equilibria. Geochim Cosmochim Acta 42: 367–375

*Chatillon-Colinet C, Kleppa OJ, Newton RC, Perkins D III* (1983) Enthalpy of formation of $Fe_3Al_2Si_3O_{12}$ (almandine) by high temperature alkali borate solution calorimetry. Geochim Cosmochim Acta 47: 439–444

*Cressey G* (1981) Entropies and enthalpies of alumosilicate garnets. Contrib Mineral Petrol 76: 413–419

*Cressey G, Schmid R, Wood BJ* (1978) Thermodynamic properties of almandine-grossular garnet solid solutions. Contrib Mineral Petrol 67: 397–404

*Davies PK, Navrotsky A* (1983) Quantitative correlations of deviations from ideality in binary and pseudobinary solid solutions. J Solid State Chem 46: 1–22

*Delany JM* (1981) A spectral and thermodynamic investigation of synthetic pyrope-grossular garnets. Thesis, University of California, Los Angeles 186 p

*Ferreira LG, Mbaye AA, Zunger A* (1988) Chemical and elastic effects on isostructural phase diagrams: the $\varepsilon$-G approach. Phys Rev B 37: 10547–10570

*Fei Y, Saxena SK, Eriksson G* (1986) Some binary and ternary silicate solutions models. Contrib Mineral Petrol 94: 221–229

*Ganguly J, Kennedy GC* (1974) The energetics of natural garnet solid solutions I. Mixing of the aluminosilicate end-members. Contrib Mineral Petrol 48: 137–148

*Ganguly J, Saxena SK* (1984) Mixing properties of alumosilicate garnets: constraints from natural and experimental data, and applications to geothermobarometry. Am Mineral 69: 88–97

*Ganguly J, Cheng W, O'Neill HStC* (1993) Synthesis, volume, and structural changes of garnets in the pyrope-grossular join: implications for stability and mixing properties. Am Mineral 78: 583–593

*Ganguly J, Cheng W, Tirone M* (1996) Thermodynamics of aluminosilicate garnet solid solution: new experimental data, an optimized model, and thermometric applications. Contrib Mineral Petrol 126: 137–151

*Gasparik T* (1984) Experimentally determined stability of clinopyroxene + garnet + corundum in the system $CaO$-$MgO$-$Al_2O_3$-$SiO_2$. Am Mineral 69: 1025–1035

*Gasparik T* (1994) A petrogenetic grid for the system $MgO-Al_2O_3-SiO_2$. J Geol 102: 97–109

*Geiger CA* (1998) A powder infrared spectroscopic investigation of garnet binaries in the system $Mg_3Al_2Si_3O_{12}-Fe_3Al_2Si_3O_{12}-Mn_3Al_2Si_3O_{12}-Ca_3Al_2Si_3O_{12}$. Eurv J Mineral 10: 407–422

*Geiger CA* (1999) Volumes of mixing in aluminosilicate garnets: implications for solid solution and strain behavior. Am Mineral (in press)

*Geiger CA, Rossman GR* (1994) Crystal field stabilization energies of almandine-pyrope and almandine-spessartine garnets determined by FTIR near infrared measurements. Phy Chem Mineral 21: 516–525

*Geiger CA, Feenstra A* (1997) Molar volumes of mixing of almandine-pyrope and almandine-spessartine garnets and the crystal chemistry and thermodynamic mixing properties of the aluminosilicate garnets. Am Mineral 82: 571–581

*Geiger CA, Armbruster T* (1997) $Mn_3Al_2Si_3O_{12}$ spessartine and $Ca_3Al_2Si_3O_{12}$ grossular garnet: structural dynamic and thermodynamic properties. Am Mineral 82: 710–718

*Geiger CA, Newton RC, Kleppa OJ* (1987) Enthalpy of mixing of synthetic almandine-grossular and almandine-pyrope garnets from high-temperature solution calorimetry. Geochim Cosmochim Acta 51: 1755–1763

*Geiger CA, Langer K, Winkler B, Cemic L* (1988) The synthesis, characterization and physical properties of end-member garnets in the system $(Fe,Mg,Ca,Mn)_3Al_2(SiO4)_3$. In: *Vollstädt H* (ed) High pressure geosciences and material synthesis. Akademie-Verlag, Berlin, pp 193–198

*Geiger CA, Lottermoser W, Amthauer G* (1990) A temperature dependent $^{57}Fe$ Mössbauer study of synthetic almandine-grossular and almandine-pyrope garnets: a comparison. Third International Symposium of Experimental Mineralogy, Petrology and Geochemistry, Edinburgh, U.K., p 11

*Geiger CA, Langer K, Bell DR, Rossman GR, Winkler B* (1991) The hydroxide component in synthetic pyrope. Am Mineral 76: 49–59

*Geiger CA, Merwin L, Sebald A* (1992) Structural investigation of pyrope garnet using temperature-dependent FTIR and $^{29}Si$ and $^{27}Al$ MAS NMR spectroscopy. Am Mineral 77: 713–717

*Gottschalk M* (1997) Internally consistent thermodynamic data for rock-forming minerals in the system $SiO_2-TiO_2-Al_2O_3-Fe_2O_3-CaO-MgO-FeO-K_2O-Na_2O-H_2O-CO_2$. Eur J Mineral 9: 175–223

*Guggenheim EA* (1952) Mixtures. Clarendon Press, Oxford, 270 pp

*Hackler RT Wood BJ* (1989) Experimental determination of Fe and Mg exchange between garnet and olivine and estimation of Fe-Mg mixing properties in garnet. Am Mineral 74: 994–999

*Haselton HT* (1979) Calorimetry of synthetic pyrope-grossular garnets and calculated stability relations. Thesis, University of Chicago

*Haselton HT, Newton RC* (1980) Thermodynamics of pyrope-grossular garnets and their stabilities at high temperatures and high pressures. J Geophys Res 85: 6973–6982

*Haselton HT Jr, Westrum EF Jr* (1980) Low-temperature heat capacities of synthetic pyrope, grossular, and $pyrope_{60}grossular_{40}$. Geochim Cosmochim Acta 44: 701–709

*Hensen BJ, Schmid R, Wood BJ* (1975) Activity-composition relationships for pyrope-grossular garnet. Contrib Mineral Petrol 51: 161–166

*Hildebrand JH, Prausnitz JM, Scott RL* (1970) Regular and related solutions. Van Nostrand Rheinhold New York, 228 pp

*Hofmeister AM, Chopelas A* (1991) Thermodynamic properties of pyrope and grossular from vibrational spectroscopy. Am Mineral 76: 880–891

*Holland TJB, Powell R* (1998) An internally consistent thermodynamic data set for phases of petrological interest. J Met Geol 16: 309–343

*Hsu LC* (1968) Selected phase relationships in the system Al-Mn-Fe-Si-O-H: a model for garnet equilibria. J Petrol 9: 40–83

*Kieffer SW* (1980) Thermodynamics and lattice vibrations of minerals. 4. Application to chain and sheet silicates and orthosilicates. Rev Geophy Space Phys 18: 862–886

*Kleppa OJ* (1976) Mineralogical applications of high-temperature reaction calorimetry. In: Proceedings of the NATO Advanced Study Institute, Newcastle, England. John Wiley, London, pp 369–387

*Kolesnik Yu N, Nogteva VV, Paukov IYe* (1977) The specific heat of pyrope at 13–300 °K and the thermodynamic parameters of some natural varieties of garnet. Geokhimiya 4: 533–541

*Kolesnik Yu N, Nogteva VV, Arkhipenko DK, Orekhov BA, Paukov IYe* (1979) Thermodynamics of pyrope-grossular solid solutions and the specific heat of grossular at 13–300 K. Geochem 79: 57–64

*Kolesov B, Geiger CA* (1998) Raman spectroscopy of silicate garnets. Phys Chem Mineral 25: 142–151

*Koziol A* (1990) Activity-composition relationships of binary Ca-Fe and Ca-Mn garnets determined by reversed, displaced equilibrium experiments. Am Mineral 75: 319–327

*Koziol AM, Newton RC* (1989) Grossular activity-composition relationships in ternary garnets determined by reversed displaced-equilibrium experiments. Contrib Mineral Petrol 103: 423–433

*Koziol AM, Bohlen SR* (1992) Solution properties of almandine-pyrope garnet by phase equilibrium experiments. Am Mineral 77: 65–773

*Krupka KM, Robie RA, Hemingway BS* (1979) High-temperature heat capacities of corundum, periclase, anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$, grossular and $NaAlSi_3O_8$ glass. Am Mineral 64: 86–101

*Martins JL, Zunger A* (1984) Bond lengths around isovalent impurities and in semiconductor solid solutions. Phys Rev B 30: 6217–6220

*Mikkelsen JC, Boyce JB* (1983) Extended X-ray absorption fine structure study of $Ga_{1-x}In_xAs$ random solid solutions. Phys Rev B 28(12): 7130–7140

*Mukhopadhyay B, Holdaway MJ, Koziol AM* (1997) A statistical model of thermodynamic mixing properties of $Ca-Mg-Fe^{2+}$ garnets. Am Mineral 82: 165–181

*Murad E, Wagner FE* (1987) The Mössbauer spectrum of almandine. Phys Chem Mineral 14: 264–296

*Newton RC, Thompson AB, Krupka KM* (1977a) Heat capacity of synthetic $Mg_3Al_2Si_3O_{12}$ from 350 to 1000 K and the entropy of pyrope. EOS 58: 523

*Newton RC, Charlu TV, Kleppa OJ* (1977b) Thermochemistry of high pressure garnets and clinopyroxenes in the system $CaO-MgO-Al_2O_3-SiO_2$. Geochim Cosmochim Acta 41: 369–377

*Olijnyk H, Paris E, Geiger CA, Lager GA,* (1991) Compression study of katoite $[Ca_3Al_2(O_4H_4)_3]$ and grossular garnet. J Geophys Res 96: 14313–14318

*O'Neill B, Bass JD, Rossman GR, Geiger CA, Langer K* (1991) Elastic properties of pyrope. Phys Chem Mineral 17: 617–621

*Ottonello G, Bokreta M, Sciuto PF* (1996) Parameterization of energy and interactions in garnets: end-member properties. Am Mineral 81: 429–447

*Pattison DRM* (1994) Are reversed Fe-Mg exchange and solid solution experiments really reversed? Am Mineral 79: 938–950

*Pavese A, Artioli G, Prencipe M* (1995) X-ray single-crystal diffraction study of pyrope in the temperature range 30–973 K. Am Mineral 80: 457–464

Pawley AR, Redfern SAT, Holland TJB (1996) Volume behavior of hydrous minerals at high pressure and temperature. I. Thermal expansion of lawsonite, zoisite, clinozoisite, and diaspore. Am Mineral 81: 335–340

Robie RA, Hemingway BS (1972) Calorimeters for heat of solution and low-temperature heat capacity measurements. Geol Sur Prof Pap no. 755, 32 pp

Robie RA, Hemingway BS, Fisher JR (1978) Thermodynamic properties of minerals and related substances at 298.15K and 1 bar ($10^5$ Pascals) pressure and at higher temperatures. Bull US Geol Sur 1452: 456 pp

Robie RA, Bin Z, Hemingway BS, Barton MD (1987) Heat capacity and thermodynamic properties of andradite garnet, $Ca_3Fe_2Si_3O_{12}$, between 10 and 1000 K and revised values for $\Delta_f G_m^0$ (298.15 K) of hedenbergite and wollastonite. Geochim Cosmochim Acta 51: 2219–2224

Rodehorst U, Geiger CA, Armbruster T (1999) The crystal structures of synthetic grossular and spessartine between 100 and 600 K and the crystal chemistry of grossular-spessartine solid solutions (in preparation)

von Saldern JC (1994) Messungen thermodynamischer Eigenschaften im System Pyrop-Spessartin. Thesis, University of Kiel, 90 pp

Skinner BJ (1956) Physical properties of end-members of the garnet group. Am Mineral 41: 428–436

Srivastava GP, Martins JL, Zunger A (1985) Atomic structure and ordering in semiconductor alloys. Phys Rev B 31: 2561–2564

Tequi C, Robie RA, Hemingway BS, Neuville DR, Richet P (1991) Melting and thermodynamic properties of pyrope ($Mg_3Al_2Si_3O_{12}$). Geochim Cosmochim Acta 55: 1005–1010

Ungaretti L, Leona M, Merli M, Oberti R (1995) Non-ideal solid-solution in garnet: crystal-structure evidence and modelling. Eur J Mineral 7: 1299–1312

Watanabe H (1982) Thermochemical properties of synthetic high-pressure compounds relevant to the earth's mantle. In: Akimoto S, Manghnani M (eds) High-pressure research in geophysics. Reidel, Boston, pp 441–464

Westrum EF Jr, Essene EJ, Perkins D III (1979) Thermophysical properties of the garnet, Grossular: $Ca_3Al_2Si_3O_{12}$. J Chem Thermo 11: 57–66

Wood BJ (1988) Activity measurements and excess entropy-volume relationships for pyrope-grossular garnets. J Geol 96: 721–729

Wood BJ, Hackler RT, Dobson DP (1994) Experimental determination of Mn-Mg mixing properties in garnet, olivine and oxide. Contrib Mineral Petrol 115: 438–448

Zhang L, Ahsbahs H, Kutoglu A, Geiger CA (1999) Single-crystal hydrostatic compression of synthetic pyrope, almandine, spessartine, grossular and andradite garnets at high pressures. Phy Chem Mineral 26 (in press)

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