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# A powder infrared spectroscopic investigation of garnet binaries in the system $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$

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**Abstract:** The powder IR phonon spectra of synthetic garnets of the six binaries in the system  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  (Pyrope - Py) -  $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  (Almandine - Al) -  $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  (Spessartine - Sp) -  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  (Grossular - Gr) have been recorded and analyzed. Between 14 and 17  $F_{1u}$ -symmetry infrared active modes were observed for the different garnet end members and can, to a first approximation, be assigned to internal  $\text{SiO}_4$  vibrations and external lattice vibrations of the  $\text{SiO}_4$  tetrahedron and the  $\text{Al}^{3+}$  and  $\text{X}^{2+}$ -site cations. This description is limited by mode mixing which is most pronounced for the lowest frequency modes. Two mode behavior is observed for  $\text{X}^{2+}$ -cation translations for most of the binaries. The site-group and factor-group splittings have been calculated for all six binaries. For the almandine/pyrope-grossular binaries, the factor-group splittings suggest that  $\text{SiO}_4$  group vibrational interactions do not change linearly between the two end-members. No evidence in the IR spectra is found for long range  $\text{X}^{2+}$ -cation order and all synthetic solid solutions are long-range disordered. The IR spectra provide information on the possible lattice heat capacities and entropies of mixing for the six solid solutions. The frequency changes of the lowest frequency external modes of pyrope-grossular and almandine-grossular garnets are consistent with the proposal of excess lattice entropies of mixing at low temperatures. The almandine-spessartine binary should be thermodynamically ideal, while the almandine-pyrope, spessartine-pyrope and spessartine-grossular binaries could show some excess lattice properties. The higher frequency modes above  $400\text{ cm}^{-1}$  of the solid solution compositions can be estimated well from a linear interpolation between the two end-members. This is consistent with the proposal that no excess lattice entropies of mixing should be present in garnet solid solutions above 300 K.

**Key-words:** garnet solid solutions, IR spectroscopy, phonon spectra, mixing properties, heat capacity, order-disorder.

## Introduction

The long-range static structural properties of the aluminosilicate garnets have been intensively investigated by X-ray and neutron scattering experiments since Menzer solved the structure in 1926. More recently, attention has turned towards investigating the microscopic and mesoscopic

scale structural properties and the dynamic structural properties using a variety of spectroscopic methods. Raman and IR spectroscopy can provide localized structural and dynamic information. The vibrational properties, that is the lattice dynamics, are revealed through the respective zone-center vibrations of both methods. Raman spectroscopy is very useful because of the

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detailed information one can obtain from polarized single-crystal spectra (Moore *et al.*, 1971; Hofmeister & Chopelas, 1991a; Kolesov & Geiger, 1997; Kolesov & Geiger, 1998). IR spectroscopic measurements using powder, thin-film and single-crystal reflectance and absorption methods have also been undertaken on garnet (see references below). The powder method is simple to apply and can yield useful structural and dynamic information, whereas reflectance spectra are experimentally more involved requiring more spectral evaluation, but ultimately yield quantitative mode frequencies, for example, as compared to powder spectra.

Most of the IR spectroscopic studies that have been undertaken on silicate garnets have concentrated on natural materials (*e.g.*, Tarte, 1965; Moore *et al.*, 1971; Tarte & Deliens, 1973; Hofmeister & Chopelas, 1991a; McAloon & Hofmeister, 1993; Hofmeister *et al.*, 1996). Hence, a need exists for systematic investigations on synthetic garnets, which are more easily characterized in terms of their chemistry and P-T history (*e.g.*, Delany, 1981; Geiger *et al.*, 1989; Lu *et al.*, 1993). We have, therefore, measured the powder IR spectra of the six synthetic garnet binaries in the system  $Mg_3Al_2Si_3O_{12}$  (Pyrope - Py) -  $Fe_3Al_2Si_3O_{12}$  (Almandine - Al) -  $Mn_3Al_2Si_3O_{12}$  (Spessartine - Sp) -  $Ca_3Al_2Si_3O_{12}$  (Grossular - Gr) to better understand the short-range, dynamic and thermodynamic properties of aluminosilicate garnet solid solutions.

### Experimental methods and limitations

The synthetic garnet solid solutions studied have been reported upon in a number of different sources. The Al-Py and Al-Gr solid solutions are described in Geiger *et al.* (1987, 1989) and Geiger & Feenstra (1997), the Al-Sp garnets in Geiger & Feenstra (1997), the Py-Gr garnets in Bosenick *et al.* (1995, 1996) and Bosenick & Geiger (1997), the Sp-Gr garnets in Koziol (1990), and the Py-Sp garnets in von Saldern (1994). These references describe the synthesis conditions and the characterization of the garnets

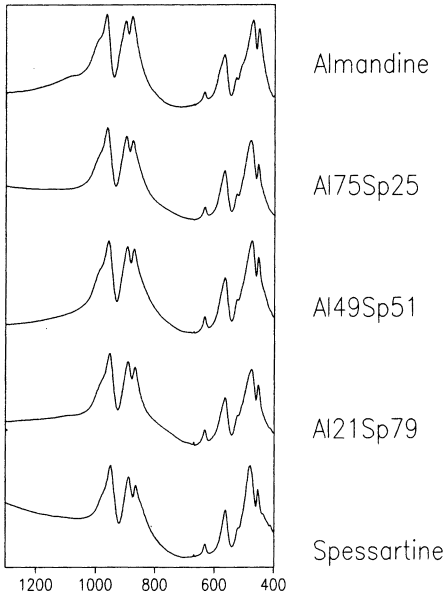
used herein. Regarding the synthesis conditions, all garnets were prepared using glass starting materials and were synthesized dry in a piston-cylinder device at elevated pressures and temperatures. The garnets are considered to be largely free of any OH<sup>-</sup> component based on their featureless IR spectra between 3700-3500 cm<sup>-1</sup>.

The garnets, which are normally polycrystalline aggregates with crystal sizes between 10 and 50 μm, were finely ground in an agate mortar. Between 1-2 mg of garnet powder were mixed with either KBr or polyethylene and pressed under vacuum into 13 mm diameter pellets. Measurements were undertaken using a Bruker X66G FTIR spectrometer for the far-infrared (FIR) region and a ATI Genesis FTIR spectrometer for the mid-infrared (MIR) region. The beam splitter was Mylar for the FIR region and KBr for the MIR. Garnet spectra between 1200 and 400 cm<sup>-1</sup> were recorded using KBr pellets and between 450 and 80 cm<sup>-1</sup> using the polyethylene pellets. A resolution of 2 cm<sup>-1</sup> was chosen with a total of 32 scans averaged for each final spectrum. In two of the series (pyrope-spessartine and almandine-spessartine) the spectra of several compositions were only recorded in either the IR or FIR region, but not both, because of lack of material.

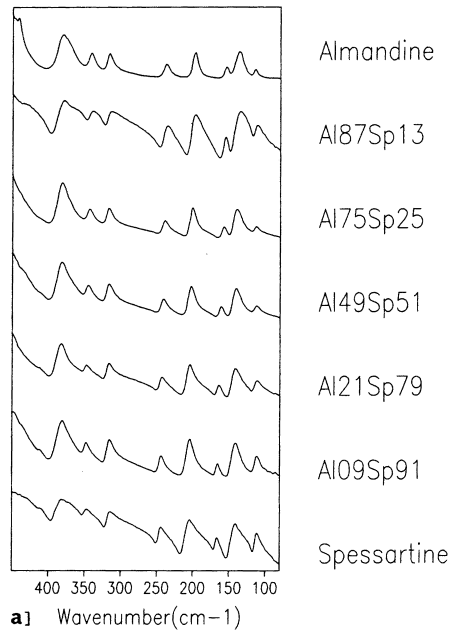
Powder IR spectra have been recorded more often on garnet (*e.g.*, Tarte, 1965; Moore *et al.*, 1971; Tarte & Deliens, 1973; Narayanan Kutty & Anantha Iyer, 1973). The main reason for this is the simplicity of the method. Quantitative information on mode frequencies can be gained from single-crystal studies using reflection or thin-film absorption spectra (*e.g.*, Hofmeister & Chopelas, 1991a). Powder spectra have several limitations. First, in a typical powder spectrum the absorption bands are a combination of transverse and longitudinal optic (abbreviated TO and LO, respectively) modes. This can result in a shifting of the TO peak position towards the frequency of the LO component. This effect can be especially pronounced for intense bands which appear in the MIR region. Weaker FIR bands are affected less. This is the reason for the differences between mode frequencies measured in

Fig. 1. Powder infrared spectra of the six binary garnet solid solutions in the MIR and FIR regions (a-f). The spectra were collected using a resolution of 2 cm<sup>-1</sup> and averaged over 32 scans. The Y-axis is in arbitrary units of absorption. The spectra are shown in the following order: a) Almandine-Spessartine garnets, b) Almandine-Pyrope garnets, c) Pyrope-Spessartine garnets, d) Almandine-Grossular garnets, e) Pyrope-Grossular garnets, and f) Spessartine-Grossular garnets.

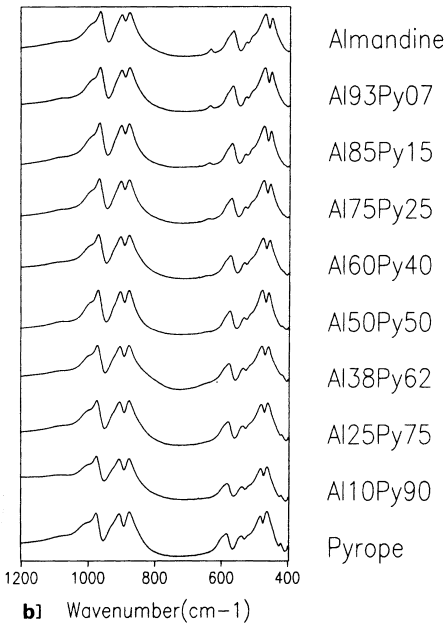
MIR bands of almandine–spessartine solid solutions



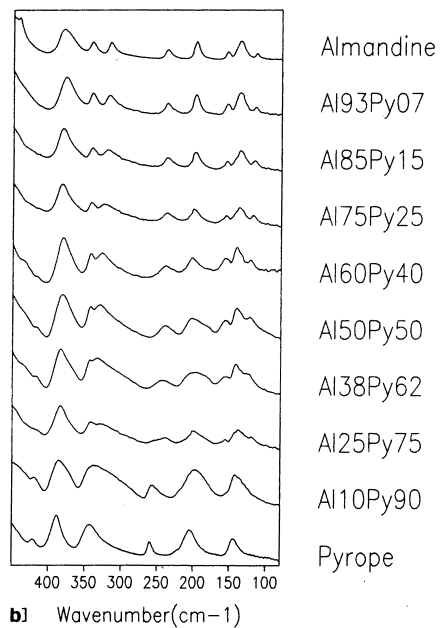
FIR bands of almandine–spessartine solid solutions



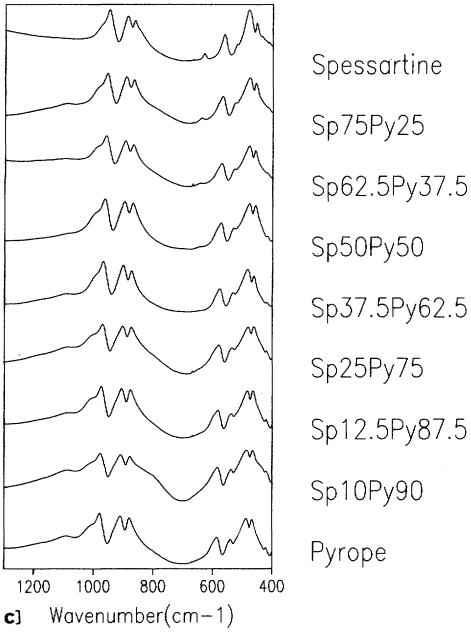
MIR bands of almandine–pyrope solid solutions



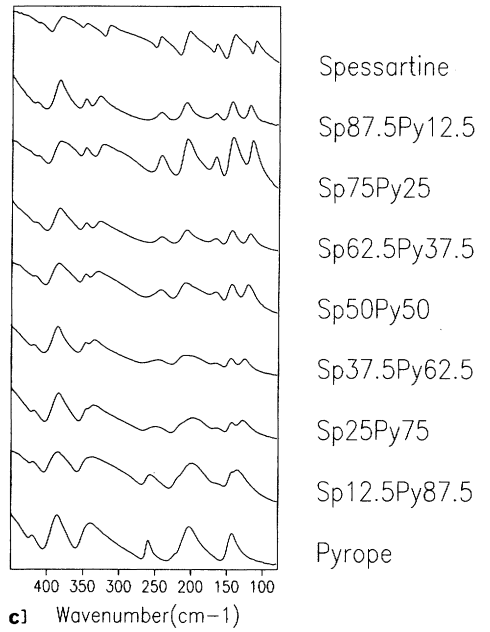
FIR bands of almandine–pyrope solid solutions



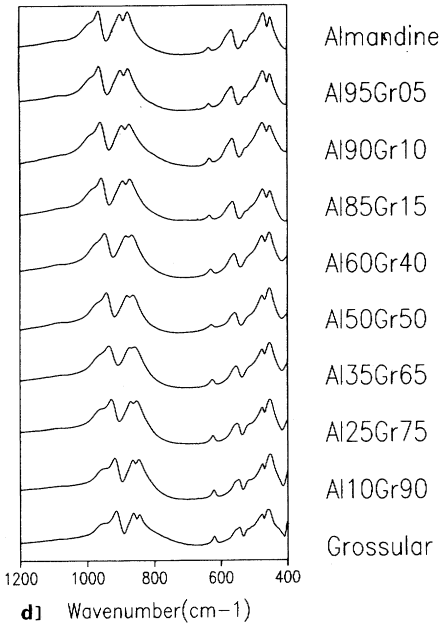
MIR bands of spessartine–pyrope solid solutions



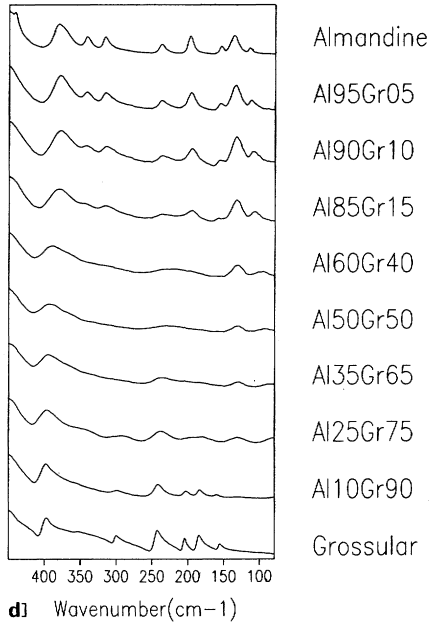
FIR bands of spessartine–pyrope solid solutions



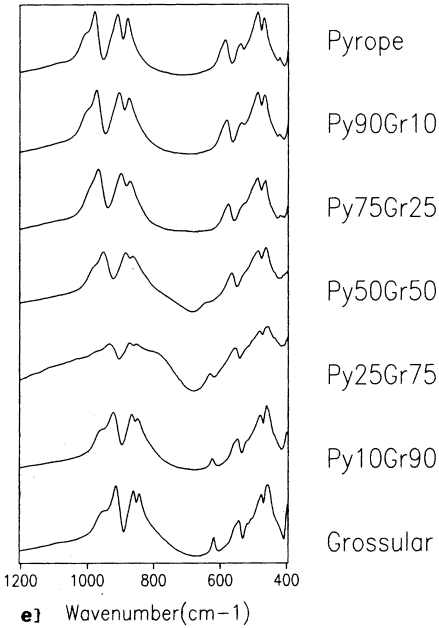
MIR bands of almandine–grossular solid solutions



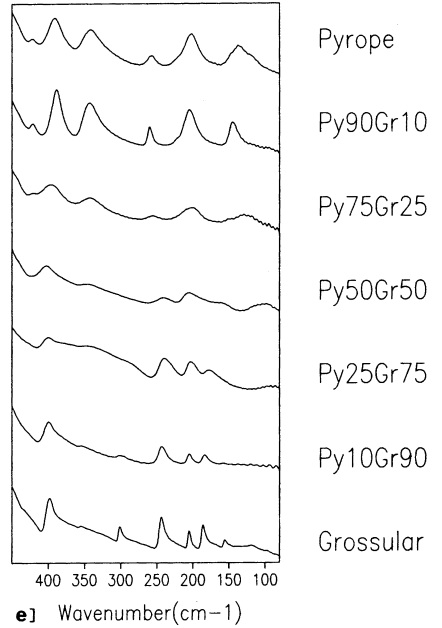
FIR bands of almandine–grossular solid solutions



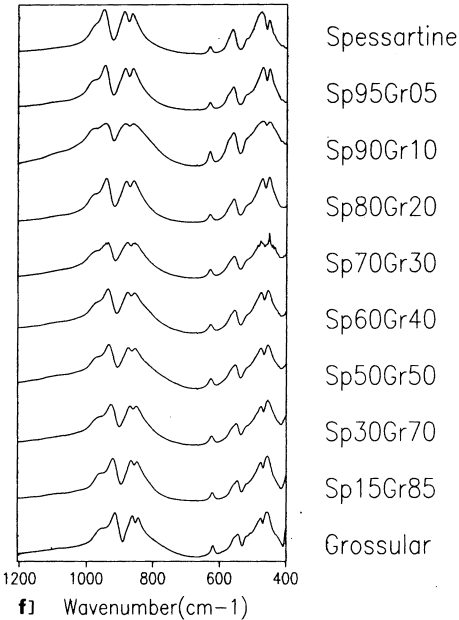
MIR bands of pyrope–grossular solid solutions



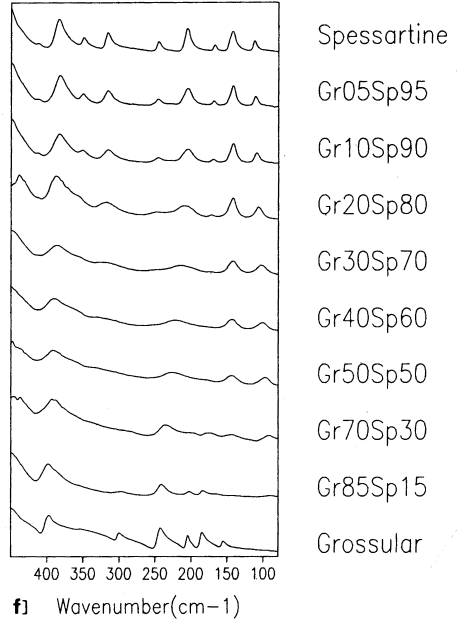
FIR bands of pyrope–grossular solid solutions



MIR bands of spessartine–grossular solid solutions



FIR bands of spessartine–grossular solid solutions



powder *versus* single-crystal reflection spectra of garnets. Second, surface modes and reflection/absorption features can in some cases occur. They do not appear to be a serious problem in the spectra presented herein.

### Structure and factor-group analysis of garnet

The general formula of the silicate garnets is  $X_3Y_2Si_3O_{12}$ . The structure has space group  $Ia\bar{3}d$ , with  $Z = 8$ . The cations are located in special positions fixed by symmetry and the oxygens in general positions (Menzer, 1928). The divalent X-site cations occupy the 24c position of  $222$  ( $D_2$ ) point symmetry, the trivalent Y-site cations the 16a position of  $\bar{3}$  ( $C_{3i}$ ) symmetry, and the Si cations the 24d position of  $\bar{4}$  ( $S_4$ ) point symmetry. Garnet, having 20 atoms in the formula-unit and 8 formula-units per cell in the I-centered cell, should have 240 total vibrations in the primitive cell, three of which are acoustic. Theoretical factor-group analysis on garnet permits the total number of vibrations and the number of Raman and infrared active modes to be calculated (Koningstein & Sonnich Mortensen, 1968; Moore *et al.*, 1971). The total irreducible representation at the  $\Gamma$ -point is given as follows:

$$\Gamma = 3A_{1g} + 5A_{2g} + 8E_g + 14F_{1g} + 14F_{2g} \\ + 5A_{1u} + 5A_{2u} + 10E_u + 17F_{1u} + 16F_{2u}$$

The  $A_{1g}$ ,  $E_g$  and  $F_{2g}$  modes are Raman active, for a total of 25, and 17  $F_{1u}$  modes are active in the infrared.

Since the three different polyhedral units in garnet have different structural properties (coordinations, bond strengths, *etc.*), an attempt can be made, to a first approximation, to assign the IR bands to either internal or external vibrations of the  $SiO_4$  tetrahedra or to the  $Al^{3+}$  and  $X^{2+}$ -site cations (*e.g.*, Hofmeister & Chopelas, 1991a). It should be stressed, however, that Cahay *et al.* (1981) have shown experimentally in an investigation employing isotopic substitution in pyrope garnet that mode mixing is present, especially in the FIR region. Therefore, strictly speaking, there can be no assignment of individual IR bands to specific atomic or polyhedral motions. Kolesov & Geiger (1998) proposed that the Raman active external modes show substantial kinematic mixing between one another (*cf.* Hofmeister & Chopelas, 1991a). This is consistent with the large number of shared polyhedral edges in the garnet structure.

## Results and discussion

### Spectra and mode assignments

The powder infrared spectra of the six garnet binaries within the system almandine-pyrope-grossular-spessartine are shown in Fig. 1a-f. The MIR bands are intense and those in the FIR are narrower and weaker in intensity. No more than 17 bands are observed in any composition and in most cases less than 17 are present. In a few cases (*e.g.*, spessartine in the spessartine-almandine solid solutions), the background is somewhat poorly behaved at high frequencies. Also some bands in a few spectra are relatively broad compared to those of other compositions in the same series (*e.g.*, pyrope<sub>25</sub>grossular<sub>75</sub> in the MIR). In several cases, bands are asymmetric or have broad shoulders, (*e.g.*, spessartine and composition almandine<sub>87</sub>spessartine<sub>13</sub> in the FIR region of the almandine-spessartine series and some of the spessartine-pyrope garnets). These features are experimental artifacts resulting probably from reflection/absorption effects, substandard grain sizes or grain-size distributions in the pellets. They do not affect significantly the determination of the peak positions (for example, the difference in peak positions in the two different spessartines from the almandine-spessartine series and the grossular-spessartine series are not more than 4  $cm^{-1}$  and most are within 2  $cm^{-1}$  of each other) or the conclusions drawn herein. Needless to say, care must be used in trying to extract information from the line widths.

Hofmeister & Chopelas (1991a) measured the single-crystal reflectance and thin-film MIR and FIR spectra of five nearly end-member natural garnets including pyrope, almandine, grossular, spessartine, and andradite ( $Ca_3Fe_2Si_3O_{12}$ ). Following upon the studies of Tarte (1965), McDevitt (1969), Moore *et al.* (1971) and Cahay *et al.* (1981), they made mode assignments for the different silicate garnets. Since their initial investigation, Hofmeister and coworkers made further studies on natural garnet solid solutions, and one synthetic join, closely approximating binary compositions. The results from these studies resulted in small modifications to the original mode assignments. Specifically, Lu *et al.* (1993) made mode assignments for spessartine, McAloon & Hofmeister (1993) for grossular, and Hofmeister *et al.* (1996) for pyrope-almandine garnets. These studies serve as the basis for the mode assignments made to the powder spectra of

this investigation. These mode assignments have been adopted so as to maintain consistency between studies, but may in the future require re-evaluation.

For the powder spectra herein, all 17  $F_{1u}$  bands were detected only in the spectrum of spessartine. For the other end-member garnets, a few modes were considered to be too weak or too strongly overlapped to be observed. The symbol T(M), where M represents a certain cation, is adopted and refers to external translations (vibrations of the  $Al^{3+}$  and  $X^{2+}$ -site cations were considered to be only translational in nature) and  $R(SiO_4)$  to a rotation.

### Mode frequencies as a function of composition

The binary solid solution which is the easiest to interpret and to assign modes is the Al-Sp join. Here, all 17 IR-active modes can be identified, with the exception of a T(Al) mode in almandine-rich compositions, which should be located slightly above  $400\text{ cm}^{-1}$  (Fig. 1a). This mode occurs as a weak band in spessartine-rich compositions and decreases in intensity with increasing almandine content. It is observed more clearly in the single-crystal reflectance spectra of Hofmeister *et al.* (1996). There is little change in energy of the 17 different IR active modes as a function of composition, because of the similarities in the sizes and masses of  $Mn^{2+}$  and  $Fe^{2+}$  ( $0.96$  vs.  $0.92\text{ \AA}$ , Shannon 1976, and  $54.94$  and  $55.85\text{ a.m.u.}$ , respectively) and, therefore, probably as well, the force constants associated with them. The mode frequencies as a function of composition across the join are displayed in Fig. 2a. The lowest frequency vibrations are assigned to mixed T( $Fe^{2+}/Mn^{2+}$ )-cation and  $SiO_4$ -group translations.

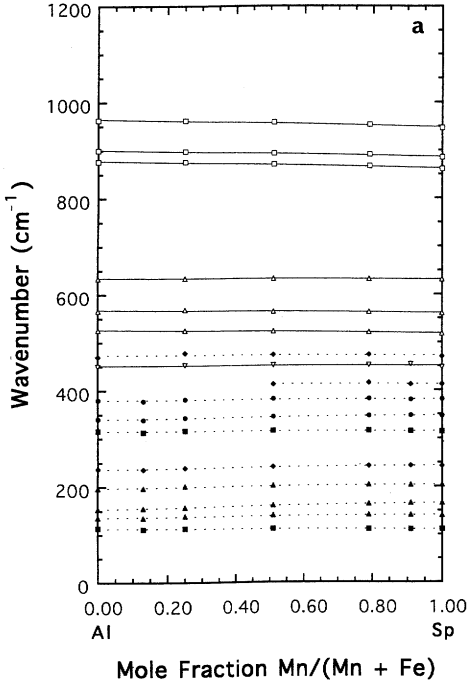
The next two joins which show the smallest changes in mode frequencies as a function of composition are the Al-Py and Py-Sp binaries (Fig. 2b and 2c). In these two binaries, complications arise because only 14 bands out of a total of 17 can be observed with certainty in pyrope-rich compositions. Hofmeister *et al.* (1996) have shown that two bands in pyrope's spectrum are accidentally degenerate. They are located at about  $145$  and  $345\text{ cm}^{-1}$  (both are labeled as T( $SiO_4$ ) modes in Fig. 2b and 2c). The evolution of these bands as a function of composition across the Al-Py and Py-Sp binaries can be traced (Fig. 2a and 2b). In addition, the weak  $\nu_4$   $SiO_4$ -bending mode located at about  $630\text{ cm}^{-1}$  in almandine- and spessartine-rich garnets cannot be

traced into pyrope-rich compositions. Therefore, the 17 IR modes can be accounted for by reference to the other end-members, assuming that no abrupt jumps in mode frequency occur. For the Al-Py and Py-Sp joins, all of the modes, except one in its respective binary, show linear frequency shifts between the two end-members. The lone exception, involving an X-site cation translation, is considered to display two-mode behavior (Hofmeister *et al.*, 1996). In pyrope this band is located around  $215\text{ cm}^{-1}$  and the corresponding mode in almandine is located at  $155\text{ cm}^{-1}$  and in spessartine around  $166\text{ cm}^{-1}$  (Fig. 2b and 2c). In the Raman spectrum of pyrope a  $F_{2g}$  mode at  $135\text{ cm}^{-1}$  has been assigned to a T(Mg) vibration (Kolesov & Geiger, 1998), whereas the T( $SiO_4$ ) modes were assigned to bands with frequencies above  $200\text{ cm}^{-1}$ . The IR mode at  $145\text{ cm}^{-1}$  in pyrope can be assigned to a mixed T( $SiO_4$ )/T(Mg) vibration keeping in line with the work of Hofmeister *et al.* (1996) and Cahay *et al.* (1981). The latter showed that this mode has a large T( $Mg^{2+}$ ) character based on its observed shift with the substitution of  $^{26}Mg$ . The results of this study, conducted with a grating spectrometer, need to be confirmed with measurements using a FTIR spectrometer. The assignment of this mode at  $145\text{ cm}^{-1}$  to a largely T( $Mg^{2+}$ ) vibration would allow consistency with the Raman results, whereby permitting the  $F_{1u}$  and  $F_{2g}$  vibrations to have similar frequencies.

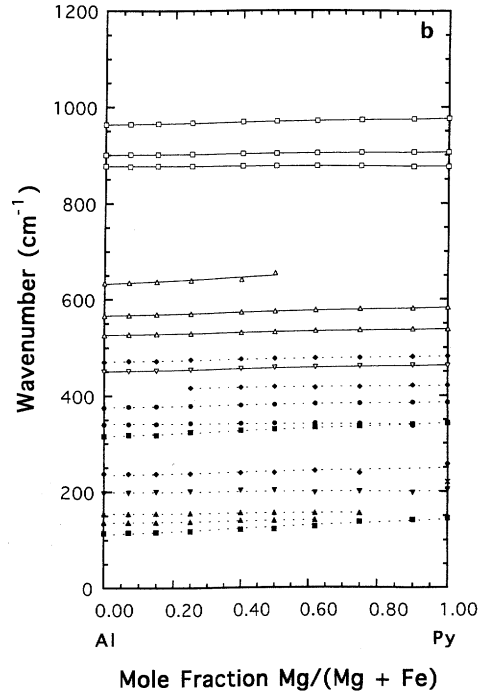
Two-mode behavior in a solid solution involving two end-members of the same structure normally occurs when the masses or force constants of the mixing cations are substantially different (Sherwood, 1972). Lattice dynamic calculations involving structures as complicated as garnet have not been undertaken and thus a rigorous physical explanation of the phenomena is not at hand. Hofmeister & Chopelas (1991a) interpreted the occurrence of two-mode behavior in garnet binaries on the basis of the large mass and size differences between the mixing X-site cations and proposed that it could be associated with vibrations other than those associated with the X-site cation translations. Kolesov & Geiger (1998), in a Raman single-crystal spectroscopic study of garnet, proposed instead that two-mode behavior occurs, in principle, only for X-site cation vibrations in aluminosilicate garnet solid solutions. In the case of garnet, the IR modes are of the same  $F_{1u}$  symmetry and they couple to a large degree, thus complicating the interpretation (Cahay *et al.*, 1981). Here the restrictions behind



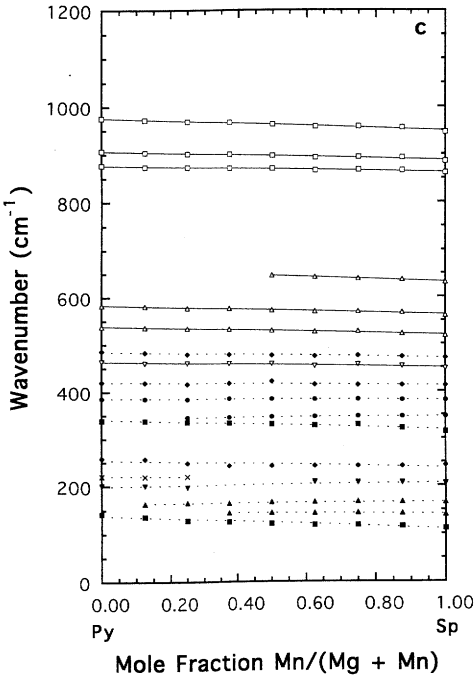
Al-Sp Binary



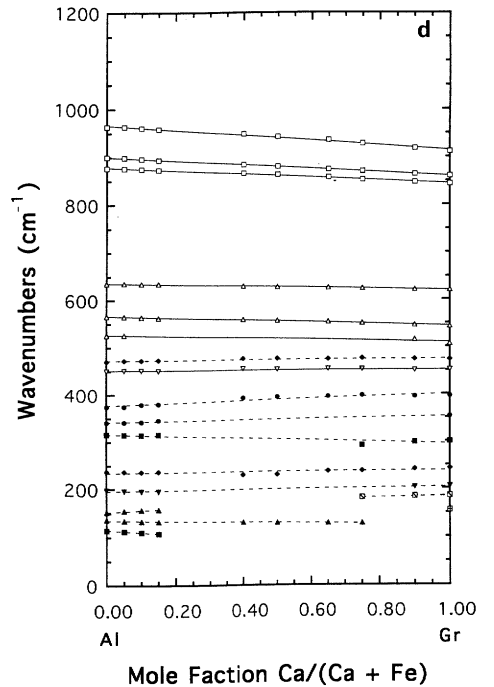
Al-Py Binary



Py-Sp Binary



Al-Gr Binary



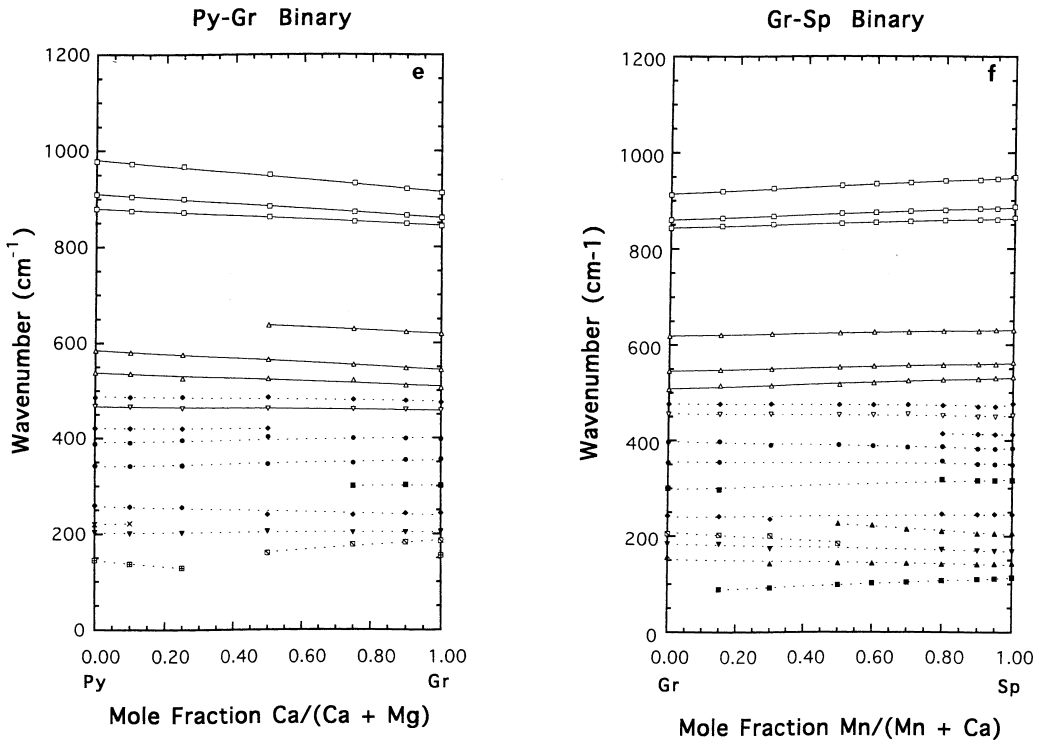


Fig. 2. Plot of the observed IR vibrational mode frequencies *versus* composition for the six binary garnet solid solutions: a) Almandine-Spessartine, b) Almandine-Pyropo, c) Pyropo-Spessartine, d) Almandine-Grossular, e) Pyropo-Grossular and f) Grossular-Spessartine. The open symbols connected by the solid lines represent internal vibrations of the  $\text{SiO}_4$  tetrahedra, where the squares correspond to asymmetric Si-O stretching vibrations,  $\nu_3$ , the open triangles to asymmetric bending vibrations,  $\nu_4$ , and the inverted open triangles to symmetric bending vibrations  $\nu_2$ . The other solid and partially filled symbols connected by dashed lines represent external vibrations and are defined as follows: the solid diamonds represent translational motions of the  $\text{Al}^{3+}$  cations, the solid circles represent rotations of the  $\text{SiO}_4$  tetrahedra, the solid squares represent translations of the  $\text{SiO}_4$  tetrahedra, the solid inverted triangles correspond to translational motions of mixed X-site cations, the normal solid triangles to  $\text{Fe}^{2+}/\text{Mn}^{2+}$ -cation translations, the crosses to Mg-cation translations, the squares with the diagonal to Ca-cation translations, and the squares with the crosses to mixed X-cation and  $\text{SiO}_4$ -tetrahedra translations.

The lines trace the frequency of a given mode as a function of composition. The FIR spectra of some solid solution compositions have bands that are so broad and weak that it was not possible to determine their frequencies.

factor-group analysis begin to break down and some modes may be best described as lattice modes and it is difficult to determine whether differences in mass or the force constants are responsible for this behavior.

In the case of the Al-Py and Py-Sp binaries, the differences in the ionic radii between  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  and between  $\text{Mn}^{2+}$  and  $\text{Mg}^{2+}$  are small being about 3 % and 7 %, respectively. The masses of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  are, in contrast, significantly heavier being more than twice that of  $\text{Mg}^{2+}$  (24.31 a.m.u.). Mass has a large effect on the vibrational amplitudes of the X-site cations

in garnet, (Geiger *et al.*, 1992; Armbruster & Geiger, 1993; Geiger & Armbruster, 1997) and thus affects significantly the mode frequencies of the  $\text{X}^{2+}$  cation vibrations (Kolesov & Geiger, 1998). In the case of IR-active vibrations, some non  $\text{X}^{2+}$ -site cation modes may not be present across the join because of the strong coupling or mixing with the X-site cation vibrations.

The temperature dependent X-ray diffraction studies have shown that the amplitudes of vibration of the X-site cations also depend on their size. The two garnet joins showing the largest mode frequency and intensity changes as a func-

tion of composition are the Al-Gr and the Py-Gr binaries (Fig. 2d and 2e). Here size and mass differences between the X-site cations play an important role in the FIR region.  $\text{Ca}^{2+}$  has a radius of 1.12 Å and a mass of 40.08 a.m.u.. For both binaries it is not possible to follow completely the FIR mode evolution as a function of composition. Mode assignments and correlations between the end members are also complicated because the IR spectrum of grossular is characterized by only 15 observable modes. A T(Al) mode, which is not observed, should be located at about 430  $\text{cm}^{-1}$  and an accidentally degenerate mode around 240  $\text{cm}^{-1}$  (shown as a T(Al) mode in Fig. 2d) consists of T(Ca) and T(Al) vibrations (McAloon & Hofmeister, 1993). The lowest frequency mode in grossular is considered to be a mixed mode consisting of T( $\text{SiO}_4$ ) and T(Ca) vibrations. This assignment is also adopted for the pyrope-rich garnets of this join (Hofmeister *et al.*, 1996 and Fig. 2d). The compositionally middle part of both joins displays broad, very weak bands in the FIR (Fig. 1d and 1e). For these two solid solutions a distribution of local modes (Sherwood, 1972), relatively well separated in frequency, should be pronounced leading to extensive band broadening. Two-mode behavior is also strongly developed, because the frequencies of the “ $\text{Fe}^{2+}/\text{Mg}^{2+}$ -related” and “ $\text{Ca}^{2+}$ -related” modes are greatly removed from one another and their corresponding dispersion curves do not overlap (*cf.* Hofmeister & Chopelas, 1991a). Similar behavior was also observed for the  $\text{X}^{2+}$ -cation translation modes in the powder Raman spectra of Py-Gr garnets (Kolesov & Geiger, 1998). In the case of the lowest frequency IR modes of the Py-Gr solid solutions, they appear to decrease in frequency compared to those found in the two end-members. The lower vibrational frequencies of the “Mg-related” and “Ca-related” translations in the solid solutions may be accompanied by increased amplitudes of vibration as described by:

$$\langle |u(j)|^2 \rangle = \frac{3k_{\text{B}}T}{m_j\omega^2} \quad (1)$$

where,  $u(j)$  is the root-mean-square value for an atomic displacement parameter,  $k_{\text{B}}$  Boltzmann's constant,  $\omega$  the angular frequency, and  $m_j$  the mass, in the general harmonic case describing an atom in a monoatomic unit-cell (Dove, 1993). The case for garnet is, of course, considerably more complicated, but this relationship could well apply to the loosely bonded X-site cations.

The remaining garnet binary, the Sp-Gr solid solution, is also somewhat difficult to interpret in the FIR region (Fig. 2f). Here the FIR modes (Fig. 1f) do not broaden as much as in the Al-Gr and Py-Gr binaries and the mode frequency shifts as a function of composition are not as extreme, but two-mode behavior appears nevertheless present. Mode broadening is pronounced in grossular-rich compositions, as in the other binaries, and complicates an evaluation of the mode behavior across the join.

### Crystal-chemical properties from the IR spectra

It appears in the case of garnet that the Raman and IR vibrational spectra can be partly interpreted using a polyhedral-based crystal chemical model and a knowledge of the X-site cation behavior (*e.g.*, Hofmeister & Chopelas, 1991a; Hofmeister *et al.*, 1996; Kolesov & Geiger, 1998). The temperature dependent X-ray refinements show that the  $\text{SiO}_4$  and  $\text{AlO}_6$  polyhedra vibrate as rigid bodies in comparison to the dodecahedra, which cannot be considered as rigid, and where the  $\text{X}^{2+}$ -site cations vibrate anisotropically in the large dodecahedral site of point symmetry 222 (Geiger *et al.*, 1992; Armbruster *et al.*, 1992; Armbruster & Geiger 1993; Geiger & Armbruster, 1997). It should be noted, however, that the X-ray data and the IR spectra deliver different information. An analysis of the X-ray determined difference displacement parameters suggests that the garnet structure can be viewed as a framework consisting of rigid corner-sharing tetrahedra and octahedra with the weakly bonded X-site cations occupying the large dodecahedral cavities. The IR spectra, on the other hand, show that only the  $\text{SiO}_4$  groups vibrate as rigid bodies. It is sometimes difficult to separate isolated external polyhedral or cation vibrations from one another in the FIR region.

The IR spectra permit some crystal chemical interpretations about the nature of the  $\text{SiO}_4$  groups. Moore *et al.* (1971) proposed that the degree of separation of two lower frequency  $\nu_3$  modes, defined as site-group splitting (SGS), is a measure of the amount of  $\text{SiO}_4$  tetrahedral distortion. The tetrahedra in garnet have  $\bar{4}$  point symmetry with two different O-O edge lengths. The SGS's, which apparently measure bond-angle distortion, for the end-member garnets are 30  $\text{cm}^{-1}$  for pyrope, 23  $\text{cm}^{-1}$  for almandine, 24  $\text{cm}^{-1}$  for spessartine and 18  $\text{cm}^{-1}$  for grossular, which is consistent with the observation that the

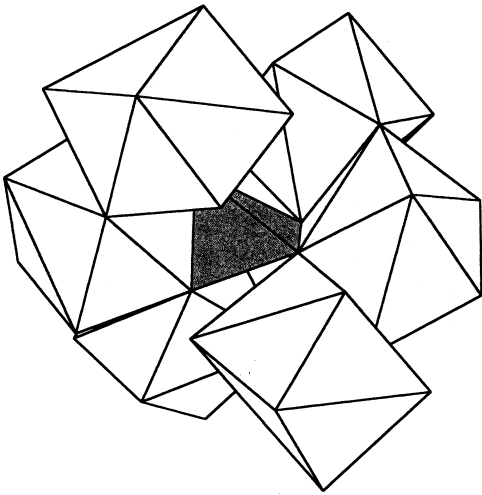


Fig. 3. Section of the garnet structure showing the polyhedral linkages between an isolated SiO<sub>4</sub> tetrahedron and surrounding dodecahedra.

tetrahedra in garnet become more regular with increasing size of the X-site cation (Novak & Gibbs, 1971). The structural relationship between a tetrahedron and surrounding dodecahedra is shown in Fig. 3. Each tetrahedron shares two edges with dodecahedra and four corners with other dodecahedra. It is this relationship which leads to the strong coupling between X-site cation and external SiO<sub>4</sub> vibrations.

In addition, Moore *et al.* (1971) also introduced the term factor-group splitting (FGS), which is defined by the relationship:  $[\nu_3(\approx 950 \text{ cm}^{-1}) - (\nu_3(\approx 900 \text{ cm}^{-1}) + \nu_3(\approx 850 \text{ cm}^{-1}))/2]$ . It proposes to be a measure of the degree of vibrational interaction between the isolated SiO<sub>4</sub> groups and increases with decreasing distance between the SiO<sub>4</sub> tetrahedra. The FGS's are 84 cm<sup>-1</sup> for pyrope, 75 cm<sup>-1</sup> for almandine, 73 cm<sup>-1</sup> for spessartine and 60 cm<sup>-1</sup> for grossular. The SGS's and FGS's for the six different binaries are shown in Fig. 4. All binaries show a linear

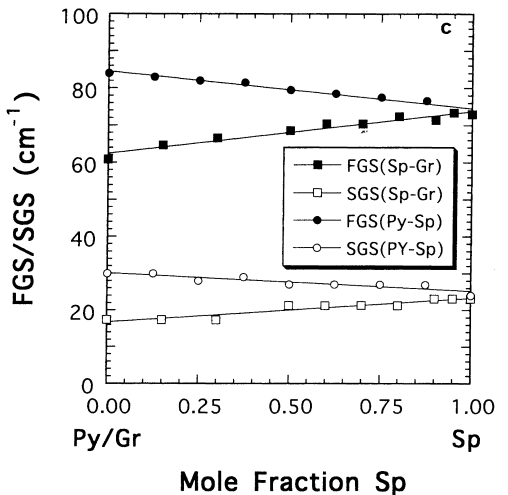
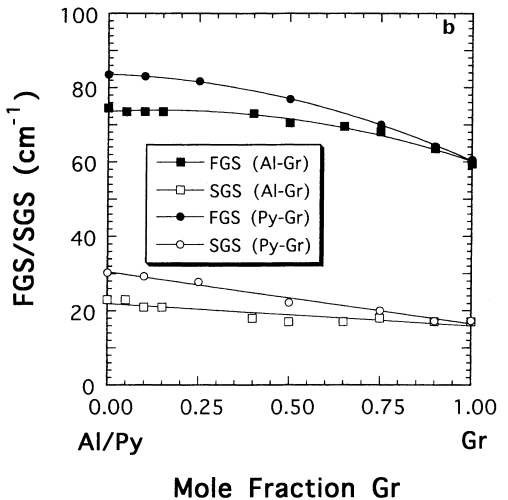
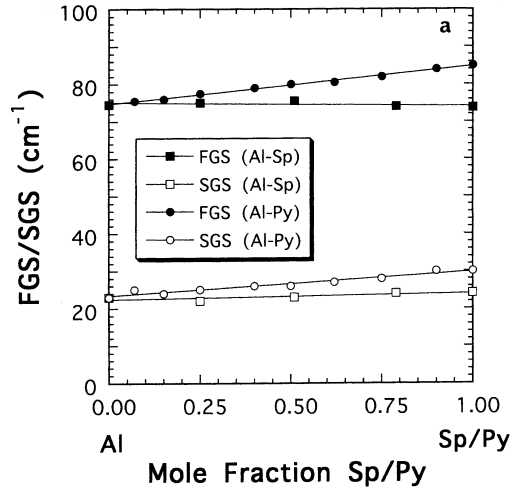


Fig. 4. Plot of factor-group (FGS) and site-group (SGS) splittings for the six aluminosilicate binary garnet solid solutions, a.) Almandine-Spessartine and Almandine-Pyrope, b.) Almandine-Grossular and Pyrope-Grossular, and c.) Grossular-Spessartine and Pyrope-Spessartine. The lines are linear or 2nd-order polynomial least-squares best fits to the data and have no physical significance.

change in the SGS's between the two end-members. The FGS's are also linear except for the Al-Gr and Py-Gr binaries, where the size differences between X-site cations are the greatest. Here, the data suggest a nonlinear trend similar to that shown by the thermodynamic excess volumes of mixing for both binaries (Geiger *et al.*, 1989; Bosenick & Geiger, 1997). Previous IR spectra obtained on natural more compositionally complex garnets suggested that the change in FGS is linear as a function of composition (Moore *et al.*, 1971; Narayanan Kutty & Anantha Iyer, 1973). The crystal-chemical interpretation is that vibrational coupling between isolated SiO<sub>4</sub> tetrahedra in the Al-Gr and Py-Gr binaries is not a linear function of composition and suggests that cation repulsions could be an important factor in affecting the volumes of mixing. In both of these joins it appears that SiO<sub>4</sub>-tetrahedral interactions do not change significantly until about 20 to 25 mole % of the larger volume component (Gr) has been substituted into the smaller volume host (Al or Py). A possible explanation for this behavior is that the larger Ca-dodecahedral sites remain "compressed" by the smaller host structure in this compositional region. X-ray absorption studies on the Ca-edge of these two solid solutions measuring the Ca-O bond lengths are required to test this hypothesis.

### Order-disorder

The question of order-disorder in garnet can also be addressed using the IR spectra. There can be no long-range cation ordering in garnet of space group  $Ia\bar{3}d$ . To date, relatively little diffraction work has been directed towards aluminosilicate garnet solid solutions to check for possible cation ordering (see Armbruster *et al.*, 1992). Most diffraction-based structural studies have concentrated on end-member compositions. The recent study of Merli *et al.* (1995) has increased greatly the number of diffraction data on garnet solid solutions, but the emphasis therein was not placed on looking for cation ordering. X-site cation ordering may only produce small changes in diffraction intensity data, which can be easily overlooked. Griffen *et al.* (1992) undertook a single crystal X-ray diffraction study of a compositionally complex aluminosilicate-rich garnet of composition,  $(\text{Fe}_{1.88}\text{Ca}_{0.75}\text{Mg}_{0.24}\text{Mn}_{0.10})_{2.97}(\text{Al}_{1.96}\text{Fe}_{0.03}\text{Ti}_{0.01})_{2.00}\text{Si}_{3.01}\text{O}_{12}$ . They reported the occurrence of slight long-range ordering of the X-site cations for the structure

refined in space group  $I4_1/acd$ . Dempsey (1980) also suggested that a synthetic garnet of composition  $\text{Py}_{90}\text{Gr}_{10}$  possessed the space group  $I2_13$ , which would allow ordering of Mg and Ca into two crystallographically independent dodecahedral sites.

The number of optic modes of a crystalline substance depends on its symmetry. Space groups lower in symmetry than  $Ia\bar{3}d$  will give rise to a larger number of IR active modes. For example, in the case of space group  $I2_13$ , a total of 58 infrared-active modes are predicted from factor group analysis (Delany, 1981). The MIR and FIR spectra of the pyrope-grossular solid solutions herein, including the composition  $\text{Py}_{90}\text{Gr}_{10}$ , do not show such a large number of IR active bands. No more than 17 bands were observed in any composition. Hence, long-range ordering of Mg and Ca does not occur in the synthetic solid-solution garnets of this study. The spectra of the other solid solutions also show no additional bands compared to the end-members and therefore, no overt evidence for long-range cation ordering is observed. Based on the IR spectra of these synthetics and the large number of spectra recorded on natural garnets (*e.g.*, Tarte, 1965; Moore *et al.*, 1971; Tarte & Deliens, 1973; Narayanan Kutty & Anantha Iyer, 1973), we find no evidence to support symmetries lower than  $Ia\bar{3}d$  for any of these aluminosilicate garnets (*cf.* Hofmeister & Chopelas, 1991a). Rossmannith & Armbruster (1995) have demonstrated the importance in correcting for the effects of "Umweganregung" in the refinement of X-ray diffraction data obtained on garnet, which was not done in many earlier studies. Griffen *et al.* (1992) did not mention if they made a correction for this effect and moreover, they did not report any additional bands in an IR spectrum obtained on their garnet. This garnet may be disordered over the correlation lengths of the IR and X-ray diffraction experiment.

Short-range ordering of the X-site cations in the aluminosilicate garnets is permitted in  $Ia\bar{3}d$  symmetry. It has been shown through <sup>29</sup>Si NMR measurements that short-range ordering of Ca and Mg is found in pyrope-grossular solid solutions (Bosenick *et al.*, 1995). They reported that there is a tendency to form Mg- and Ca-rich clusters around a tetrahedron (Fig. 3) in pyrope- and grossular-rich solid solutions, respectively. The effect of short-range ordering on the vibrational spectra of garnet has not been investigated, but should in principle be discernible

through hard-mode infrared spectroscopy investigations (e.g., Güttler *et al.*, 1989).

### Implications for heat capacities and third-law entropies of mixing

It is the phonon density of states which determines the heat capacity of a substance. The heat capacity gives the third-law entropy *via*:

$$S_T^0 = \int_{0K}^T (C_p/T) dT \quad (2)$$

There exists no experimental determination of the phonon density of states, obtained *via* inelastic neutron scattering, for the silicate garnets. Artioli *et al.* (1996) have measured the dispersion relations for acoustic phonons along several high-symmetry directions across the Brillouin zone of a natural nearly end-member pyrope, but no optic phonons were measured. IR and Raman spectra give information on the optic modes at the Brillouin zone center and can be used, together with additional data and certain assumptions, to calculate lattice heat capacities (Dove, 1993; Kieffer, 1979; 1980). Hofmeister & Chopelas (1991b) made  $C_p$  calculations for end-member pyrope and grossular using their IR and Raman data (Hofmeister & Chopelas, 1991a) and the Kieffer model. Their model  $C_p$ 's for grossular reproduce the experimental data fairly well, but not in the case of pyrope (Fig. 5). The heat capacities are underestimated at low temperatures (for example, about 9 J/Mole-K around 100 K accounting for about 15 % of the total heat capacity at this temperature) and overestimated at high temperatures (about 10 J/Mole-K at 1000 K). The calculated  $C_p$ 's are dependent, of course, on their assigned model density of states, which will require reformulation using new Raman mode assignments (*i.e.* Kolesov & Geiger, 1998). At the present stage of development, it remains to be demonstrated if lattice dynamic calculations based solely on IR and Raman spectra can give quantitative information on the lattice heat capacities of mixing for garnet solid solutions, inasmuch as the maximum amount of nonideality in the heat capacities of mixing should be less than 25 % based on measurements on Py-Gr garnets (Haselton & Westrum, 1980; Bosenick *et al.*, 1996).

The IR phonon spectra of this study permit, however, a qualitative analysis of how the  $C_p$ 's and lattice entropies of mixing may behave for

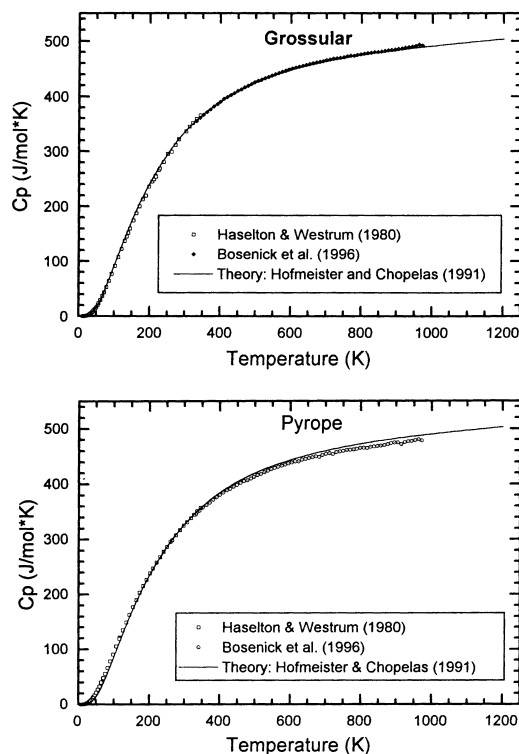


Fig. 5. Heat capacity of grossular and pyrope as a function of temperature from 10 to 1000 K. The symbols are the experimental data and the solid lines represent the Kieffer-based model calculations of Hofmeister & Chopelas (1991b).

the different binary garnet solid solutions, assuming they are representative of the entire phonon density of states. IR spectra offer, therefore, an additional source of information on the lattice entropies of mixing complementing or checking estimates made through conventional thermodynamic modeling of phase equilibrium results (e.g., Mukhopadhyay *et al.*, 1997). Based on the linear change in IR mode frequencies along the Al-Sp binary, it is to be expected that this binary should have ideal lattice heat capacities of mixing. At the other extreme, the Py-Gr and Al-Gr binaries, which show shifts of the low frequency modes to even lower frequencies for the solid solution compositions compared to the analogous modes in the end-members, should show substantial excess heat capacities of mixing at low temperatures. In the case of the former binary, this has been verified experimentally (Haselton & Westrum, 1980). The most simple

lattice dynamics explanation for the excess heat capacities is that the small Mg cation increases its amplitude of vibration in expanded dodecahedral sites in the solid solution compositions, thereby lowering its frequency of vibration relative to Mg in end-member pyrope (eqn. 1). This should increase the heat capacity of the solid solution at low temperatures compared to a mechanical mixture of Py and Gr of the same composition, as it is the low frequency optic modes that contribute most heavily to  $C_p$  at low temperature (Kieffer, 1979, 1980).

The Gr-Sp binary should also possess measurable deviations from ideal thermodynamic mixing for the same reason. The remaining two joins, Al-Py and Py-Sp, which contain mixing cations of similar sizes, but of significantly different masses, show two-mode behavior. They have relatively linear frequency shifts in the low-energy region. Because of the two-mode behavior, the phonon density of states could be different for solid solution garnets relative to a mechanical mixture of the same bulk composition. They may have small excess lattice heat capacities of mixing at low temperatures.

The linear changes in frequency of the MIR modes between the end members for all of the solid solutions above  $400\text{ cm}^{-1}$  support the hypothesis that the heat capacities of mixing at temperatures above 300 K are thermodynamically ideal. Experimental  $C_p$  measurements between 300 and 1000 K on Py-Gr garnets support this proposal (Bosenick *et al.*, 1996).

Predictions of the thermodynamic mixing behavior of silicate solid solutions systems have normally been interpreted in a static way, based largely on the sizes of the mixing cations (*e.g.*, Kravchuk, 1981) or the differences in volume of the end-member components (Davies & Navrotsky, 1983). A consideration of the masses of the mixing cations, and hence the dynamics of the solid solution phases, has not been made. Static-based crystal chemical models are too simple to be correct in describing quantitatively the lattice entropies and free energies, because it is the lattice dynamics which control them. In order to properly understand the thermodynamic mixing properties and systematics of a given mineral or structure group, their dynamic properties will have to be addressed. In the case of garnet, further vibrational spectroscopic studies should be made at low frequencies, where the mode frequencies are related to the vibrational behavior of the X-site cations. Calorimetric investigations

should also focus on low-temperature measurements, where nonideality in the solid solutions appears to be originating.

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